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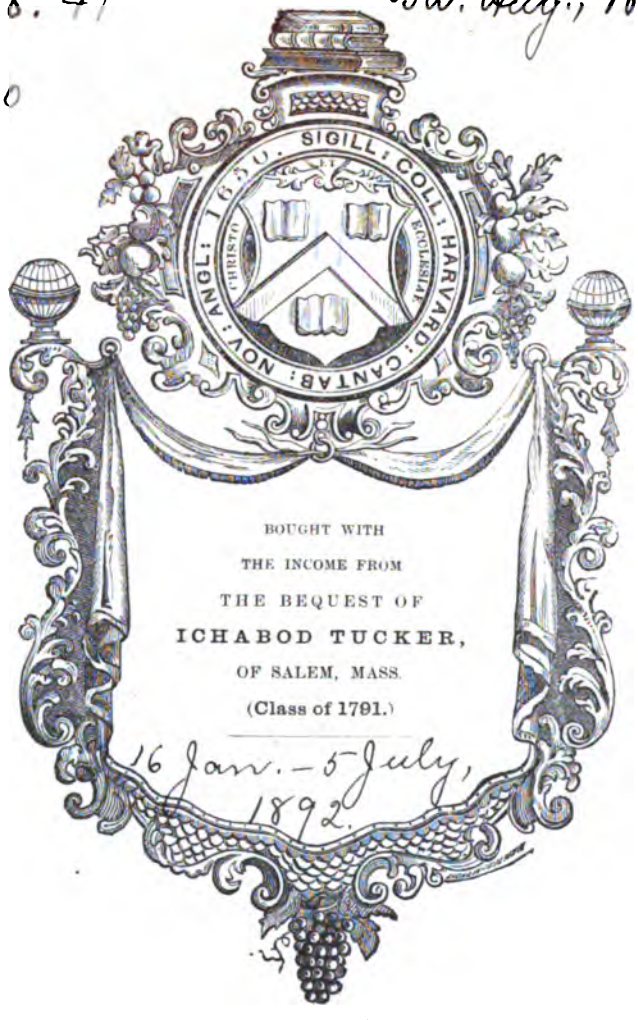

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VOLUME LXV.—1892.

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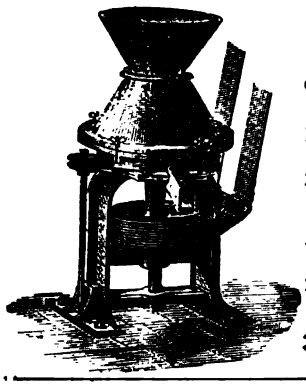

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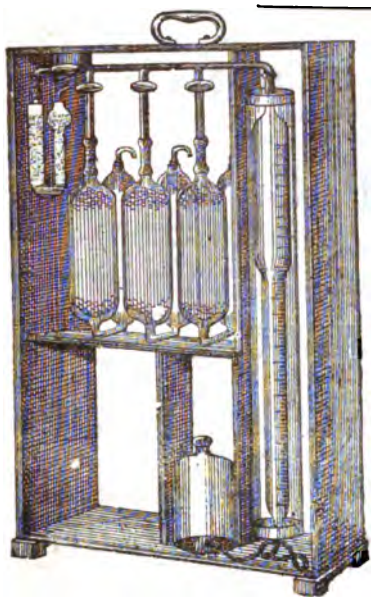

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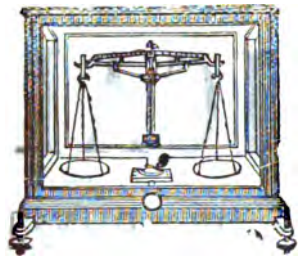

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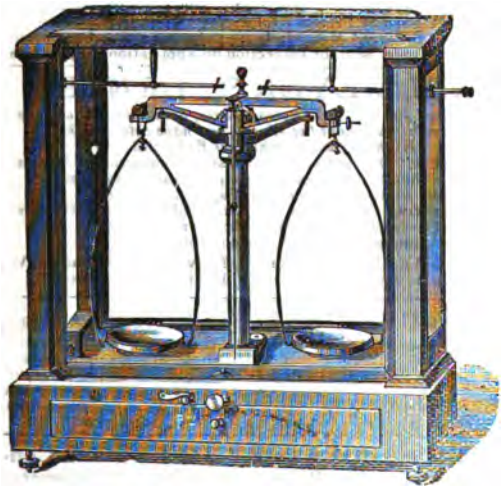

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VOLUME LXV.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1675.—JANUARY 1, 1892.

ON THE

DETERMINATION OF THE MELTING POINTS OF MINERALS.*

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., B.E., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

THERE appears to have been no serious attempt made in recent times by mineralogists to effect the determination of the melting points of minerals with a degree of accuracy in keeping with our present means of measuring high temperatures. Nor has there been any suggestion, to the best of my knowledge, as to the possibility of providing a simple and accurate means of observation. The present paper (preliminary to one embodying the melting points of the more abundant mineral species) is occupied with an account of a method of effecting such determinations which it is hoped possesses qualities of simplicity and accuracy. It will be seen that its use necessitates only the most minute quantities of the substance, and hence the method is applicable for dealing with rare mineral species or small quantities of chemically prepared bodies; other applications of the method besides the determination of melting points are suggested in this paper.

In meeting the expenses connected with the development of the apparatus, I have to acknowledge thankfully a grant made to me by the Royal Irish Academy.

The scale of fusibility of Van Kobell is still quoted in the most recently published mineralogical works. It constitutes a comparative method, beset with errors, even as a means of identification, save under special circumstances. Thus whether a splinter of a mineral will melt in the flame of the blowpipe depends as much, or more, on the shape, conductivity, and dimensions of the splinter as on its melting point. For example, a filament of the fibrous actinolite is more easily fused than a fragment of the compact orthoclase. The melting point of actinolite is, however, some 100° Centigrade above that of orthoclase. Again, the chemical action of the flame may sometimes interfere. But not alone do these sources of error arise in comparing the behaviour of substances in the blowpipe flame, but the scale of Van Kobell is itself highly irregular in its spacing, and even erroneous in the order of fusibilities. Thus the melting and softening points in Centigrade degrees of specimens of Van Kobell's standards, as determined by the method to be described later, are as follows:—

		Melting. °C.	Softening. °C.
1.	Stibnite	525	—
2.	Natrolite	965	—
3.	Almandine	1265	972
4.	Actinolite (green)	1296	971
5.	Orthoclase	1175	865
6.	Bronzite (Diallage)	1300	—
7.	Quartz	1430	—

The numbers prefixed give the order of fusibilities as ordinarily given for Van Kobell's scale. The wide difference observable between the temperatures at which softening may be first detected and those at which melting, in the ordinary sense of liquefaction, is attained, is due to the viscosity of the substances. Unfortunately, this property of viscosity appears, to a greater or less degree, common to the mineral silicates, and is most conspicuously displayed in the case of quartz itself. It is, of course, impossible to assign any quite definite melting or softening point in such cases, whatever the method of determination adopted. There is no sudden change of state. A fact well shown in the curve of the thermal capacity of melting basalt recently determined by Professors Austen and Rücker (*Phil. Mag.*, vol. 32, p. 353). Possibly the temperature corresponding to the upper bend of the curve when the latent absorption appears nearly or quite complete should, in accordance with the facts attending the liquefaction of non-viscous bodies, be defined as the melting temperature. A point apparently a little below 900° C. in the case of basalt. But the temperature is not well defined. In connection with what is said above as to the possible chemical effects of the blowpipe flame, it is interesting to notice further that Professors Austen and Rücker observe upon discrepancies introduced into their experiments, apparently traceable to the chemical action of the flame, whether reducing or oxidising, used in effecting the meltings.

From present experience, it appears as if the high degree of viscosity possessed by silica, where this body constitutes a considerable constituent of a substance, may have the effect of masking the influence on the melting point of small variations in the percentages, or in the nature, of the bases present. To what extent this will prove to be the case future experiments must decide. That it should be so at all is unfortunate for many purposes of determination. But it is at least certain that the melting or softening intervals of a viscous mineral substance may be rendered of far higher discriminative and scientific value than is attained by use of the blowpipe method of determination. In the case of non-viscous bodies, such as halite, stibnite, &c., a definite temperature or melting point is readily found by the method described in this paper. The terms "melting

* A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

point" and "softening point," as applied to viscous bodies in this paper, are defined further on, as well as the mode in which they are determined.

The "Meldometer" (μελδω, I melt), as I have designated the instrument used in determinations of melting-points, is of the following construction:—A ribbon of pure platinum, having a width of about 1·2 m.m., is stretched between forceps, furnished each with a binding screw, and insulated from each other so that on connecting the binding screws with a battery a current can be passed through the ribbon. Upon the surface of this ribbon the substance to be examined is placed. It is necessary first to reduce the mineral to a fine powder in an agate mortar, and finally grind it with a little water till in the form of a fine fluent paste; a speck of this is *spread* over a small area of the ribbon. The best condition for observing melting is when a few particles are *thinly* spread here and there upon the platinum. A quantity invisible to the unassisted eye may be dealt with, for in all cases the phenomena of melting are observed through a microscope. The microscope having been brought to bear upon the *thin* coating of the powdered mineral upon the platinum, a current of gradually increasing intensity is passed through the ribbon till the mineral melts or volatilises. In this process the mineral often exhibits very characteristic phenomena. It remains to describe how the temperature of the platinum ribbon at the moment at which the mineral melts may be determined. Commencing, however, with the simplest form of the apparatus, I proceed to describe a form of the meldometer with which observations, *directly* comparative between the substance being investigated and other substances of known melting-points, are effected. In cases in which identification is the object in view, we compare the behaviour of the substance with that of the species to which we think it referable from its other characters.

Simple Form of the Meldometer.

Fig. 1 shows, to half real scale, a plan and side elevation of this form of the meldometer intended to rest on the stage of a microscope.* It consists of two forceps—one insulated—attached to a disk-shaped brass plate. This latter may be held down on the stage of the microscope by the stage clamps, and is placed so that the ribbon stretched between the forceps is brought to traverse the field of view. A one-inch foreign objective of cheap pattern is suitable for this work. I have had one in use for some years, and it seems uninjured. These powers have single lenses. If a compound cemented objective is used, the Canada balsam used in the cementing melts if observations be prolonged at the higher temperatures. The forceps holding the ribbon close by their elasticity, and are opened by the small screws threaded into the upper member of each forceps. The ribbon is shown cut away where it is held by the forceps. This is done with a scissors before inserting it. The object is to secure a more uniform temperature over the length of the ribbon, which otherwise diminishes rapidly in temperature approaching the forceps by reason of thermal conductivity, the effect being intensified by decreased electrical resistance where the ribbon is colder. The effect of reducing the section is to diminish this loss of heat by conduction, and at the same time the electrical resistance increasing with diminished cross section up to the forceps causes a development of heat which augments as the cold metal of the forceps is approached. In this way the loss of heat to the forceps is made good, and the central parts of the short strip made more uniform in temperature. Exact uniformity of temperature throughout is not needful, for the method is one of comparison, and if the substances being compared are brought to adjacent portions of the ribbon, it may be assumed they are under like conditions as regards temperature.

The length assigned to the ribbon is conveniently about 2 c.m. A storage cell or a couple of Grove cells will furnish sufficient current to raise to a blinding white heat and finally fuse the ribbon. The current is regulated as follows:—Two rods of carbon, 51 c.m. in length, 17 m.m. in diameter, such as are used for electric-arc lighting, having each a resistance of about half an ohm, are clamped at their ends upon a piece of board. A sliding-piece consisting of two sprung brass tubes encircling each carbon, and connected by a cross-piece of brass, can be moved along from end to end of the carbons. At one end the carbons are each furnished with a binding screw, and are insulated from one another save where connected by the sliding-piece. This resistance is placed in circuit with battery and meldometer, so that the current flows through more or less of the carbon rods according to the position of the slider. Thus, the total resistance in circuit may be varied by moving the latter, and in this way the quantity of current traversing the circuit controlled. Having placed the two substances to be compared side by side, we can thus expose both to any temperature up to that at which the platinum breaks. It will be found that quartz may be melted before this point is reached, and reduced to a glass which no longer affects polarised light. At these high temperatures the

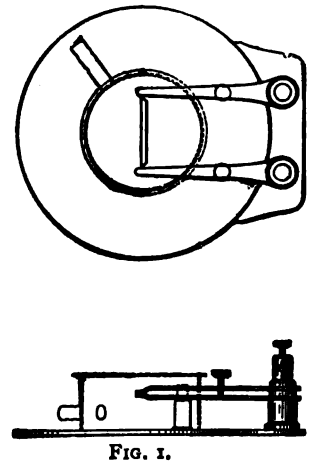

Fig. 1.

light is very intense, and it is necessary to shield the eye from its effects. A cover-glass smoked over a lamp flame may be placed above the eye-piece of the microscope, but a small piece of neutral tinted glass, such as is used in snow spectacles, is better for the purpose.

When the platinum is heated in this form of the meldometer, as the forceps are fixed in position, the expansion results in considerable sag of the ribbon. This, however, is only an inconvenience in so far as it necessitates re-focussing the microscope upon the object. By making one of the forceps free to rotate on a vertical axis at the binding screw, and affixing a weak, spiral controlling spring, so that the ribbon is always distended by a small force, this inconvenience may be avoided, or the distance of the forceps apart may be adjustable by a screw (see figure in the *Journ. Royal Micros. Society*, x., p. 1068); but the simpler form of the apparatus is preferable.

Employment of the Simple Meldometer.

If we seek to identify the body, of course we ultimately compare it with accredited specimens of the body we suspect it to be; and here, even if infusible below the melting-point of the platinum, information is often gained by comparing the behaviour of the substances. Often, again, the phenomena which precede fusion, accompany it, or succeed it, are of much determinative value. Thus topaz blisters on the surface, glassy bubbles forming and

* This form has been already noticed briefly in *Nature*, xxxiii., 1885, pp. 15, 16. See also *Journ. Roy. Micro. Soc*, x., p. 1068. A further notice of the meldometer is reported from a paper read before the British Association at Bath, 1888, in *Industries*, vi., p. 20.

breaking up which throw out viscous threads and emit a gas (fluorine?) which attacks the platinum, forming coloured rings upon the bright red metals: iolite turns milk-white. The presence of any considerable quantity of calcium oxide produces this latter effect. Labradorite may be distinguished from the other felspars by this phenomenon. Orthoclase at high temperatures develops large bubbles—which seldom break—throughout the clear viscous liquid into which it is transformed. Tourmaline boils easily, often with effervescence at first, ultimately settling into a quiet boil. Pyromorphite flows into an oily-looking liquid, part of which runs along the ribbon till it attains a cooler region near the forceps, where it pulsates backward and foward,—a surface tension phenomenon. On cooling it is seen that a double-coloured slag is produced as if a separation had been effected. Molybdenite sublimes, building up a frail, skeleton-like structure over the ribbon, which consists of glistening, tabular, colourless crystals. These again re-sublime to similar crystals if tumbled back upon the platinum.

Some substances show a change of colour when first heated, as realgar, which blackens, and beryl, which bleaches. Some remain viscous to the last and have no definite melting-point, but gradually soften. Beryl is a case of this, and the felspars, in a less degree, possess the property. Other minerals break down comparatively suddenly and flood the platinum, as garnet, tourmaline, &c. Finally, the colour of the melted mineral—whether a slag or a glass—affords distinctive characters as in the blowpipe, but in a more extended degree inasmuch as the range of temperature is greater under perfect control, and the method more cleanly in use, uncomplicated by secondary effects, and the substance is under much better conditions for observation.

As regards the determination of melting-points in Centigrade degrees by the use of this simple form of apparatus, the closeness with which we can approximate to a true estimate depends on our ability to map out the range of temperature at our command with reliable and sufficiently varied standards of reference. As the construction of such a table or scale of melting-points should be based upon the widest possible experience, I do not suggest any complete scale here; but in the second part of this paper will endeavour to rectify the omission.

Meanwhile, it will be found on reference to Carnelley's "Melting and Boiling-Point Tables," or the "Tabellen" of Landholt and Börnstein, that a wide choice exists of comparative substances up to a certain range of temperature, from the determinations of Violle, Carnelley, and others on metals and pure salts. The scale will have to exclude as far as possible substances which undergo a period of viscosity before decisively melting. To such substances no definite melting-point can, of course, be assigned, and the temperature at which they begin to soften is not well defined.

If direct observations of the phenomena progressing upon the hot platinum be resorted to, we obtain for viscous bodies temperatures of melting much above, often by some hundreds of degrees, the softening point, *i.e.*, a point at which particles soften sufficiently to adhere to the platinum. In fact the earlier stages of softening appears still attended with an amount of rigidity competent to delay any considerable displacement of the lower particles an indefinite time. A much higher temperature is required to cause these lower particles to liquefy and permit of the spreading of the mass. This is the state of things when fusion becomes visible. The lower particles are then in such a state of aggregation as to yield to a small distorting force within a small interval of time. This appears to be a truly fluid state, and I have called it the melting point or melting interval. Thus if the temperature is such that within three or four minutes we perceive the finer dust rounding into little drops the melting point is attained. The temperature of softening is defined as that at which the lower particles begin to adhere to the platinum. It is evident that this will only occur when their original configuration is broken up. These particles are, of course, those most nearly at the temperature of the platinum. To determine this interval we proceed as follows. When the substance has been exposed for four or five minutes to a particular temperature, the current is stopped and the cool ribbon washed with a sable-hair brush moist with water. A high power—a half-inch is suitable—is then brought to bear upon the site of the powder. Glassy fragments adhering to the platinum indicate that a temperature not lower than the softening point has been attained. After three or four trials the softening range is determined within sufficiently narrow limits. In these trials a very small quantity of the substance may be used, as a high and good power is permissible, no observations being made while the ribbon is heated. The microscope-tube should be simply racked up while heating is going on, so that, when the current is stopped and the ribbon cleaned, the site of the powder may be formed with certainty by again bringing the objective into focus.

In the case of non-viscous bodies the temperatures of softening and melting sensibly coincide. There is instant breakdown and flooding upon the platinum.

(To be continued.)

A TABULAR EXPRESSION OF THE PERIODIC RELATIONS OF THE ELEMENTS.

By HENRY BASSETT.

At the present time the Periodic Law of the Elements is becoming universally accepted as the basis of the study of their relative properties and individual peculiarities; and Prof. Mendeleeff's tabular arrangement is very generally adopted for its illustration in modern chemical books. Having been for some time past much interested in the subject, I have been impressed with many anomalies in the table in question, some of which are generally known and admitted; but as I venture to think I have arrived at a more comprehensive and satisfactory expression, I will point out some few of the anomalies to which I refer.

At the first glance we cannot help being struck by the great blank space in the fifth column. We have no indication of the existence of any metals between Ag and Au downwards, which is at least very remarkable; the same may be said as to the platinum metals, which have been very thoroughly investigated, and are always associated in nature, but only the six are known.

According to their atomic weights, many of the so-called rare earth metals should find their places here, but their properties are absolutely incompatible with such a position, as was pointed out by Crookes in his address to the British Association in 1886, from which I will quote the following:—

"Judging from my own researches, it is probable that many of these earthy elements will be found included in one or more interperiodic groups, whilst . . . the elements between Ag and Au, Cd and Hg, In and Tl, &c., &c., are still waiting to be discovered."

Another difficulty occurs with Yb, one of the least basic earths, which follows La, the most powerfully basic of all; we also see Di, forming a strongly basic oxide, separating Nb and Ta. Again, we find U, which, like the earth-metals, can only be obtained by reduction of its chloride by sodium, allied to W, which is reduced by hydrogen at a red heat.

I will now call attention to the following table, which, with its derivatives, seems to meet the difficulties to which I have briefly alluded, and which simply amounts to an alteration in the position of Mendeleeff's ninth group, and the addition of one interperiodic group.*

* Though at present we actually know but three of these interperiodic groups, it seems not unreasonable to regard them as the *raisons d'être* of the large periods, acting as connecting links between the component small periods.

The position of the Li group at the left of the Na group may be seen in the table at page 464 of the Second Supplement to "Watts's Dictionary of Chemistry," and has quite recently been independently and ably advocated by Dr. Jas. Walker (Chem. News, 1891, lxiii., 251).

The atomic weights are Prof. Clarke's, to the first decimal, except in the case of three or four rare elements which are not included in his table of Dec. 6, 1890.

Table I.

							Cs 133		226?
							Ba 137		?
							La 138·2		?
							Ce 140·2	Th	232·6
							Ndy 140·8		?
							Pdy 143·6	U	239·6
							148?		241?
							Sm 150		?
							?		?
							?		?
							154?		248?
							?		?
							Tb 159·5		?
							Ho 162		?
							?		?
							Er 166·3		?
							169?		263?
							Tm 170·4		
							?		
							Yb 173		
			K	39·1	Rb	85·5		174?	
			Ca	40	Sr	87·6		?	
			Sc	44	Y	89·1		?	
			Ti	48	Zr	90·6		?	
			V	51·4	Nb	94	Ta	182·6	
			Cr	52·1	Mo	96	W	184	
			Mn	55		100?		189?	
			Fe	56	Ru	101·6	Os	191·7	
			Ni	58·7	Rh	103·5	Ir	193·1	
			Co	59	Pd	106·6	Pt	195	
Li	7	Na	23	Cu	63·4	Ag	107·9	Au	197·3
Be	9	Mg	24·3	Zn	65·3	Cd	112	Hg	200
B	11	Al	27	Ga	69	In	113·7	Tl	204·2
C	12	Si	28·4	Ge	72·3	Sn	119	Pb	207
N	14	P	31	As	75	Sb	120	Bi	208·9
O	16	S	32·1	Se	79	Te	125		?
F	19	Cl	35·5	Br	80	I	126·9		216?

Beginning at the lower part of Table I., we find that the gap between the two columns of most closely allied elements extending from Nb and Ta downwards, has disappeared. Yb no longer follows La, and U is far removed from W. Going upwards from Ta, we find several of the rare earth-metals, partly included in two interperiodic groups (see quotation from Crookes above), and finally we arrive at Cs, whose unknown neighbour on the right will probably be still more electro-positive, while F, at the bottom left-hand corner, is the most electro-negative of the elements.

The atomic weights indicated for some of the yet unknown elements are only introduced as probable approximations, arrived at by a comparison of the average horizontal and vertical numerical differences between the known elements in the other periods. A similar reservation must be understood as to the actual positions assigned to some of the rare earth-metals, our knowledge on these points being as yet scanty. It would seem, however, that the table provides rational positions for many, or possibly for all, of these perplexing elements, some of which may be found to have atomic weights higher than any known at present. In this case an extension of the table is, I believe, possible, but this may well be left to the future.

I must now give a quotation from Professor V. von Richter's "Inorganic Chemistry" (p. 247 of the third American edition):—"The series 5 and 6 are very incomplete; the elements Tb, Sm, and Er, little investigated as yet, will probably find places in them. It may be, however, that the two series will together form a single period of somewhat varying character."

The positions assigned to Cs, Ba, &c., apparently arbitrarily removed from their proper places adjoining Rb, Sr, &c., seem to introduce a new anomaly; but this also disappears on further examination, while the fact that Cs, though it has the lowest melting point, and is presumably the most easily volatile of the alkali-metals, can only be prepared by electrolysis of its cyanide (Setterberg, *J. C. S.*, 1882, xlii., 464), while the hydrates of Na, K, and Rb are reduced by distillation with carbon, points to a very marked difference in its character and position. The reduction of Ba is also very difficult in comparison with Ca or Sr.

If we cut out a strip of paper on which this table has been written, and roll it round a cylinder whose circumference is equal to ten of the vertical spaces, beginning at the bottom, we produce a series of derived tables of considerable interest. The first of these is simply the lowest portion of the primary table as it stands. It will be seen that the elements in the three lower lines show very complete analogies, and a regular gradation in properties from left to right, while in the four upper lines this is by no means so clearly perceived.

The second fold of the paper round the cylinder covers up all but the two left-hand small periods, and gives rise to the following;—

Table II.*

Li	Na	K	Rb	?
Be	Mg	Ca	Sr	?
B	Al	Sc	Y	?
C	Si	Ti	Zr	?
N	P	V	Nb	Ta
O	S	Cr	Mo	W
F	Cl	Mn	?	?

Here for the first time we see Na removed from its old anomalous place by Cu, while Mg, Al, and Si also find far more congenial neighbours in Ca, Sc, and Ti than when in their old positions. The compounds of the three following elements, P, S, and Cl, show also some considerable analogies with those of their new allies, *e.g.*, the phosphates and vanadates, the sulphates and chromates, and the perchlorates and permanganates, but the general resemblances are less apparent.

(To be continued).

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 315).

How indeed can we hope to understand such a chemism? It almost seems as if the idea of protoplasm is incomprehensibly deliquescent. Fortunately, however, there exists no small number of facts which encourage us to attempt the solution of the problem. The most promising way seems to us to be to bring forward, for comparison, the manner of occurrence of complicated syntheses and transformations which are sometimes characterised as "anomalous reactions," and to seek out what is common to these phenomena and to the transformations of protoplasm.

Here belong especially certain so-called condensations, indeed, generally speaking, syntheses effected by means of a third body which does not enter into the ultimate product, and which have been too little physiologically noticed. "If we," say Roscoe and Schorlemmer, "pass

* In this and the two following tables, the atomic weights are omitted for brevity.

methyl chloride into the mixture of aluminium chloride with benzol, hydrochloric acid is given off, and there is chiefly formed durol or tetramethylbenzol. Toluene, if similarly treated, yields dimethylbenzols, trimethylbenzols, tetramethylbenzols, pentamethylbenzol, and hexamethylbenzol. . . . What part is played by aluminium chloride in these complicated reactions we do not know."

We give an example that many more complicated syntheses are effected in chemical industry in presence of condensation processes, and not as mere by-reactions, but with a remunerative yield. If we treat dimethylaniline with phosgene, in presence of aluminium chloride, we obtain tetramethyldiamidobenzophenon. This body can be further condensed with other bases by the addition of condensing agents, *e.g.*, with phenyl-α-naphthylamine, and there then results α-naphthyltetramethyltriamidotriphenylcarbinol, a base the double salt of which is the Victoria blue, a colouring matter highly valued for cotton-dyeing. In many condensations the reactions are so complicated that we are left completely in the dark.

Chemistry has hitherto been content resignedly to put forward a few very doubtful and mutually contradictory equations of reaction (Friedel and Crafts; Gustavsen), but without a single attempt to obtain a clear insight into the quite peculiar conditions, and, consequently, into the peculiar forces in such condensations, which cannot be in any manner explained by chemical affinity.

Sulphuric acid, in which the especially strong by-reactions which have nothing whatever in common with condensation indicate more complicated relations, cannot be here drawn prominently into consideration, the rather as it is now rarely used in the condensation of colouring matters. But Menschutkin has shown even for "quite indifferent" solvents that strong by-reactions must occur in consequence of their solvent power, even if we leave out of account the chemical reactions which arise. These solvents are falsely named "indifferent," as the reactions are undoubtedly connected with their chemical nature.

Condensation agents, such as aluminium chloride and bromide, zinc chloride, sodium disulphide, phosphoric anhydride, possess two characteristic attributes common to them all:—

1. They all rank among the most highly hygroscopic substances.

2. In their anhydrous state they are exceedingly porous.

As hygroscopicity is common to all porous bodies a relation must exist between these two properties.

In comparison with the above-mentioned condensations may be adduced one—and indeed the simplest—of such unexplained transformations discovered by chemical industry, *i.e.*, the process for obtaining chlorine by passing dry gaseous hydrochloric acid and dry air over heated bricks. This process was indicated by Oxland in 1847. Here we cannot doubt but that the effective substance is the third porous body, the action of which, as subsequently shown by Deacon, can be much heightened by impregnation with metallic salts, especially copper sulphate. As Deacon's process comes into action only at temperatures exceeding 200°, at which temperature copper sulphate is rendered anhydrous—a circumstance which is here pointed out probably for the first time—the active body in this simple but astonishing chemical transformation is a highly hygroscopic and porous body.

Of what nature are the forces which are capable of calling forth all these mighty transformations even in the most stable compounds?

According to Bunsen, the tension in fine films of water, on fine glass tubes, amounts to hundreds of atmospheres, whence is explained the exceedingly strong absorption and condensation of carbon dioxides in such films. According to Joulin, ammonia is absorbed by wood charcoal with a tension of 246 atmospheres.

(To be continued).

NITROHYDRIC ACID.*

By TH. CURTIUS.

(Continued from p. 314).

After the solution has become cold the substance appears in shining colourless needles of a centimetre in length deceptively similar to those of lead chloride, but which if gently heated explode with fearful violence. On prolonged boiling in water, the lead salt is very gradually decomposed with the separation of a lead compound which is not explosive. By holding over it a glass rod, on which is placed a drop of a solution of silver nitrate, it may be plainly seen that nitrohydrogen is being volatilised as the drop is rendered turbid by the deposition of silver nitrogen. Nitrogen lead dissolves readily in hot acetic acid, and is gradually decomposed with liberation of nitrohydrogen. It is insoluble in concentrated aqueous ammonia.

Nitrogen Sodium, N_3Na.

This compound is obtained by neutralising the free acid with soda-lye, by adding sodium hydroxide to the ammonium salt, and concentration on the water-bath. It is most conveniently obtained by the action of sodium alcoholate upon benzyl nitrogen in an alcoholic solution.

$$C_6H_5CON_3 + C_2H_5ONa = N_3Na + C_6H_5CO_2C_2H_5.$$

The salt may be re-crystallised from water, or precipitated by adding alcohol to the aqueous solution. In order to determine the proportion of nitrogen in this compound it is necessary to burn it mixed with lead chromate.

	Calculated for N_3Na.	Found per cent. I.	Found per cent. II.
N_3 42	64·62	64·70	—
Na 23	35·58	35·29	35·62
65	100·00	99·99	—

Nitrogen sodium is readily soluble in water, but insoluble in ether and alcohol. It has a slight alkaline reaction and a very saline taste. It does not explode on percussion, but only if heated to a very high temperature. It burns with brilliant yellow light and a faint detonation.

Nitroammonium, N_4H_4.

This salt, as it is above described, is directly obtained by saturating an alcoholic solution of diazohippuramide with ammoniacal gas—

$$C_6H_5CONHCH_2CONHN_2OH + NH_3 = C_6H_5CONHCH_2CONH_2 + N_4H_4 + H_2O.$$

Ether precipitates pure nitroammonium. This compound can be re-crystallised from boiling alcohol. The proportions of nitrogen and hydrogen were conjointly determined by combustion with copper oxide in a current of carbon dioxide. The water which is formed is absorbed in the chloride of calcium tube. Extraordinary caution must be used on account of the great volatility of the substance. But even if perfectly dry carbon dioxide is passed very slowly through the apparatus, the volume of hydrogen obtained is often deficient.

If we endeavour to burn nitroammonium in a current of air in presence of copper oxide, the apparatus is invariably shattered with a fearful detonation. 0·1 grm. of the substance destroys a platinum boat, only a few flattened splinters being left. The compound sublimes at first very finely from the boat into the colder combustion tube. As the temperature rises the crystals are converted into yellow drops. As soon as this point is reached the explosion follows in a few moments. It is conceivable that the compound N_6 is first formed by oxidation and then explodes with extreme violence.

The composition of this substance is:—

	Calculated for $N_4H.NH_3$.	Found.
NH_3 17	28·83	28·00

(To be continued.)

* *Berichte der Deutsch. Chem. Gesell.*

THE PURIFICATION OF WATER.*

By Professor ALBERT R. LEEDS.

Comparing the composition of the waters obtained on the 2nd of May, at noon, from the Genesee River at Elmwood Avenue Bridge, and that from the conduit at Mount Hope reservoir, Professor Leeds stated that the water from the Genesee River had a slight yellow colour, due to peaty matters in solution, and was slightly turbid. It had a flat taste and a slight odour. That from the Mount Hope reservoir was colourless, but manifested a whitish turbidity; it was pleasant to the taste and had no odour. The Genesee water contained 0·044 of a grain of free ammonia per gallon; the Hemlock, 0·032. The Genesee water contained of albuminoid ammonia, with organic nitrogen, 0·071 of a grain; the Hemlock, 0·078, slightly more. The Genesee water required to oxidise the organic matter, 0·147 of a grain of oxygen, the Hemlock Lake, 0·136 of a grain, or something less. The difference was due to these peaty organic matters in solution, which require a slightly greater amount of oxygen to oxidise them. The hardness of the Genesee water was 6·85 grains; the Hemlock Lake, 3·2. The total solids in solution in the Genesee water were 16·47 grains; in the Hemlock Lake, 5·08 grains. A count of the bacteria contained in the waters showed that there was in the Genesee River water 112 colonies of bacteria to the cubic centimetre; in the Hemlock Lake, 63 colonies. The samples were sent to me in jugs labelled 1 and 2, and at the time of making the analysis I did not know to which samples the numbers referred. The analysis showed that No 1, the harder water, of course, came from the river. And I shall now label these bottles containing a portion of that water. And, in the first place, there is the Genesee water. Mr. President, you will notice this limpid matter in it. Perhaps you can see it.

After making the analysis, for reasons which I will explain presently, I added to each water a grain of sulphate of alumina, and then filtered the samples through sand. This marked No. 1 is the filtered Genesee water; 2, the filtered Hemlock. I do not think that it is possible to notice any difference. Both of these samples are as entirely limpid, entirely colourless, as the purest distilled water that I could make in my laboratory. They are absolutely devoid of any colour and any odour. The whitish opalescence, or the whitish turbidity, has been removed from the Hemlock water; the yellow from the Genesee water.

This brings me to the treatment of waters by filtration. And at the outset I would like to say that I know of no method by which it is possible to render waters organically pure except by filtering; and, in the second place, I know of no practical method of bringing about that result except by the American system of mechanical filtration and purification. As these statements appear strong and unqualified, I think it is important that I should briefly review the history of our knowledge and practice during the course of the past ten years, in relation to this subject.

Some six years ago there was, I think, but one city in the United States which attempted to filter its water, and that was Poughkeepsie on the Hudson. At the present day there are more than one hundred, and the practice is increasing very rapidly. In England, and on the continent of Europe, the practice of filtration is well nigh universal. Some five years ago Jersey City and Newark, in New Jersey, requested me to visit the various water supplies, in England more especially, to study this matter of filtration of their waters, and I found that all the great cities, with the exception of Glasgow, filtered their water supplies. The most conspicuous example is London, with its population of five and a half million of people. Its water supply is almost entirely taken from the River Thames, and that river receives the drainage of a very great population. The towns are compelled, by Act of Parliament, to purify their sewage to a certain point, but a great deal of filth finds its way into the Thames. By Act of Parliament the several water companies that supply London are compelled to filter their water; and to effect that object they have filter basins which cover more than a hundred acres in area. Their method of filtration is to run the water into large reservoirs containing sand. The sand that does the filtering is about two feet in depth, and supported on a substratum of coarse stone. As the filth is removed it accumulates in a thin layer upon the top of the sand; and when the water—which filters only under the pressure of the four feet, or thereabouts, of water standing in the reservoir—filters too slowly, they are compelled to send a force of men into the filter basin, shovel off the top layer of sand and dirt, remove it, wash it, and restore it to the filter bed. The same plan is followed at Berlin and other great cities on the Continent.

How the Filter Beds do their Work.

It is easy to see how they remove the dirt, the gravel, and the suspended matter; but how do these shallow basins of sand remove the living organisms—those organisms with which you are all so familiar under the name of bacteria; those organisms which, when they produce typhoid and other fevers, are known as disease germs? That operation was a complete mystery until the last four or five years. But few people had ever seen or examined bacteria before that period. It is entirely a new topic in this country; and the method by which they were removed from the waters was a profound mystery. It now has been shown that the bacteria remove the bacteria. The bacteria in the waters are comparatively few of a dangerous character; the great bulk of them are our greatest friends. It is through their aid, together with the oxygen of the air, that the filth in the water is destroyed. They feed upon it, and they feed upon each other. Since that knowledge has been obtained, the object now is to cultivate the bacteria. In order to make the filter bed do its work effectively, it is necessary that the growth of the bacteria shall be facilitated until a filter bed becomes populated with an incredible number of millions of them. As the result of their activity they multiply themselves in vast numbers; and they form, at the top of the filter beds and between particles of sand, a sort of jelly or slime—a bacteria jelly; and it is by the aid of this bacteria jelly that the bacteria in the unfiltered water are removed. The bacteria come down into the pores of the filter, when they are caught by this jelly and they are consumed. And if the rate of movement of the water is slow enough it is possible to begin with water like that of the River Spree, which is a portion of the water supply of Berlin, containing 100,000 of bacteria to the cubic centimetre, and after passing through one of the filter beds the water which comes out will contain but forty or fifty bacteria. This takes place when the rate of filtration is such that 1,000,000 gallons of water pass through those filter beds per acre in twenty-four hours. If the rate is diminished until only 300,000 gallons pass through in that interval, the bacteria can be diminished until there are only five or ten per cubic centimetre. But this rate is too slow to permit of the economical use of the filter beds, and the consequence is that the authorities of Berlin require that the water shall pass through the filter beds at the rate of a million gallons per acre in twenty-four hours. The interesting fact is thus brought out that some of the foulest water, most polluted with sewage, is so filtered at the present day in the capital of Germany; the filtered water is submitted to the most searching criticism of Professor Koch, whose institute of hygiene is there, and to whose labour our knowledge on this subject is mostly due, and

* An Address delivered by Professor Leeds before the Chamber of Commerce of Rochester, N.Y., May 12, 1891.

that this foulest of water is there taken, filtered, and then becomes the water supply of Berlin. If we can do as well or better than that, we have every reason to be satisfied that we are on the side of safety.

The foreign filter beds, excellent as they are, have never been introduced practically in the United States. Moreover, there is no prospect that they will be. The amount of water filtered per acre is so small that the first cost is a large one. In the second place, the climate of Europe and of England is altogether different from the climate of America. Those filter beds freeze up, even at London, and the engineers are sometimes greatly troubled. In the next place, in England, even in that temperate climate, a great quantity of Algæ develop in the filter beds. In the United States, with our severe winters and the great trouble you have experienced in Hemlock Lake, from the growth of Algæ, engineers are unwilling to undertake such method of filtration. This being the case, the attention of engineers has been directed to find some way of effecting a result which will satisfy our own needs. And the system that I shall bring to your notice in reference to your immediate wants is this American system.

The filter is simply a case made of boiler iron, of 5 ft., 10 ft., or 20 ft. in diameter, made strong enough to stand any pressure to which it is subjected. It contains a bed of sand 3½ or 4 ft. in depth. The water is passed through the filter under pressure, and passes out of the bottom by a series of valves so constructed that they permit the water to pass, but entirely detain the sand. After a time, when the filth accumulates on the surface and through the bed of the sand, the operation is reversed, a current of filtered water under pressure is sent up from below, the sand is washed, and the impurities pass out from a waste pipe, and then filtration is resumed. In practice, after filtering for ten hours, a filter operating on such water as the Genesee River can be purified by washing in ten minutes' time.

That it is possible by such a method to renovate the sand and dirt you will probably have no difficulty in admitting; but what will such a filter do with reference to the bacteria? If it is necessary to pass water at so slow a rate where the pressure is as light as that given by a head of four feet, as is the case in the foreign filter bed, how is it possible to pass the vastly greater quantity through one of these American filters? One of these filters of which I have been speaking, ten feet in diameter, under a pressure of 15 lbs. to the square inch, will filter successfully a quarter of a million of gallons per diem. In order to effect that result it is necessary to have something which will take the place of the bacteria jelly that I have described. And the most successful substitute is a jelly made of hydrate of alumina. It is obtained in this way. All natural water contains in solution carbonate of lime, to which its hardness is due. When sulphate of alumina is introduced into the water it is decomposed by the carbonate of lime, and sulphate of alum is formed and hydrate of alumina is set free. It is a perfectly white translucent jelly. It forms on the surface of the filter bed in contact with the grains of sand, and when the smallest particle of silt or the bacteria come in contact with it they are caught by it and held. It is possible to entirely remove the bacteria from water by use of this jelly. These filters, worked in that manner, have been repeatedly tested, and that point has been most carefully established.

The water that I have sent around the audience this evening is filtered water. It contains no bacteria. They were removed at the same time that the turbidity and the colour were taken out. The question then is, whether the bacteria are to be removed by a bacteria jelly or by means of an alumina jelly. There are some who think that no chemical substitute whatsoever can rightly be employed in the purification of water. It appears to me to adopt such a sentiment is to renounce the advantages which the very elaborate study of this question has given to us. They say that hydrate of alumina, which is one-fourth of alum, is very pernicious to health. If alum ever went into your water supply I would concede the point that it is not a proper thing to use; but it does not go into the filtered water. The alum is so perfectly decomposed that I never have been able to find it in the filtered water. The hydrate of alumina is left behind, and the alumina which goes into your water in a minute amount is also present in natural water itself. If you examine the analysis of the river water you will find that the water contains naturally some alumina. It is the alumina in the soil which makes spring water so bright. It is the alumina in the soil which makes the water of driven wells filtered water. All that is proposed in this method is to take advantage of Nature's methods.

In the sample that is before you a quarter of a grain of alum has been used. That is so small an amount that it is difficult to weigh it upon a druggist's balance. Of that quarter of a grain of alum, only one-third is alumina; and one-twelfth of a grain of alumina, or the 1-700,000th part of the weight of a gallon of water, is sufficient to remove all the dirt and all the bacteria by this process of filtration. The quantity is practically infinitesimal.

Unfortunately, the Genesee water, at the time it was sent to me, was in a very favourable condition. I wish it had been at its worst, because the difference is too slight to show what the process is capable of doing. This method is now in use supplying filtered water in much larger quantities than what you desire to have here. The City of Chattanooga, some four years ago, began taking some three million gallons of water from the Tennessee River. It has now gone on increasing its filtering plant, until it takes six million gallons, and it is all treated by the method I have spoken of. I have here a sample of water taken from the Wabash River at Terre Haute. It is not possible that the Genesee River should ever have water of the character that you see here. It is loaded with mud. The water was so bad that I at first thought, when this sample was submitted to me, that it was a hopeless case. I am interested in this question, as a consulting chemist, from the fact that a great many waters are submitted to me by the people that are engagaged in doing this work, and I am desirous of seeing this American system introduced generally. I think it will be universal before many years have passed. And here is one of the samples that was submitted. A plant was put in some year and a half ago to filter this Terre Haute water. The impurities were so great that I said that they could not be successfully handled without using as much as four grains of alum to the gallon. They have been filtering not three, but four and a half million gallons of water with a three-million-gallon filter plant. And this has been done with two grains of alum to the gallon, and less. The superintendents have been careful not to use more than that, because of the expense. They use less. And this is the largest amount of alum I have ever known to be used practically in the filtration of water.

I will not detain you longer than by saying I have here a working drawing, showing ten of these vertical filters, ten feet in diameter, which are doing this work at Terre Haute. The water is filtered under a pressure of two hundred pounds, and the filtered water is used for fire purposes as well as for general supply.

Here is the working drawing of a plant at a place in Kansas: a smaller plant. It is the same size as that at Bordentown, in New Jersey. Long Branch has for the past three years filtered and treated all its water in that way. It was much more deeply coloured with peat than the Genesee River water was that came to me, or, it is possible for the Genesee ever to be coloured. It came from a Cypress swamp. And the filtered water at Long Branch is colourless. And when the health inspector of Providence examined that plant he found that the filtered water contained two bacteria per cubic centi-

metre, while the unfiltered water contained three hundred.

In conclusion, then, I will say that this method is in use in one hundred of our American towns; that those who are using it are extending their plants to supply the increased demand; that by its use in the filtered samples which I have shown you, the organic nitrogen in the Genesee water was cut down to one-half the amount usually present, and also the water in the Hemlock Lake was cut down by the same amount. The Hemlock water, if filtered by this method, would be 100 per cent purer than delivered to you as it is, and you consider it, as it is, very excellent water.

At the recent convention of the engineers in Philadelphia the expression of opinion was general that this method of treatment of waters was, in the near future, to be generally adopted. When the city of Liverpool put in its new water supply from Vyrnwy Lake, the purest water they could obtain in Wales, they put on the descending main a filter plant; and I said to the chief engineer at Liverpool, "Why do you filter this beautiful mountain water?" and he said to me, "The public opinion in England is so strong in this matter that we cannot supply water unless it is filtered." If you have examined one of those filter systems you will find that all of the filtered water is passed through a well, at the bottom of which there is a pavement of white porcelain, and the engineer and the people are not satisfied without, on looking through a depth of five feet of water, the filtered water should always go over that porcelain and be absolutely colourless. I think the time has gone by in this country when people will be satisfied with taking any water supply without they are made certain of its purity. As I said before, I know of no method of guaranteeing the purity of water except by filtration.

Mr. President, I trust I have been not too lengthy, I wished to answer the question which was asked: "If a temporary supply of 3,000,000 gallons of water is taken from the Genesee River, can it be made colourless? —can it be made pure from a sanitary standpoint?" I have answered that it can be, and that the method is one in large use, and is a method requiring so moderate an outlay that it has become feasible for the water supply of cities demanding a great amount of water.—*The Stevens Indicator*, viii., No. 42.

ON THE DECOMPOSITION OF MINERALS CONTAINING TITANIUM.

By JESSE JONES.

In attempting to conduct the analysis of a very refractory mineral containing titanium, magnesium, chromium, &c., according to the method given by Chatard (*Journal of Analytical and Applied Chemistry*, v., 163), it was found very difficult to secure complete decomposition of the mineral by the use of hydrofluoric and sulphuric acids as detailed. Repeated fusions with potassium pyrosulphate while decomposing the mineral introduced large quantities of salts, and was very tedious.

These difficulties led me to seek some method that would give more satisfactory results. The following was finally adopted: 2 gms. of the mineral were placed in a pressure bottle, to which was added 20 c.c. of water and 20 c.c. of strong sulphuric acid. The ground-glass stopper not fitting air-tight, a small sheet of pure rubber was interposed. The bottle and contents were placed in an ordinary air bath, and kept at 200° C. for two hours. The residue weighed 0·018 grm., and was mainly silica. On treatment with hydrofluoric acid, but 0·002 grm. of residue remained. A temperature of 200° C. was found to melt the rubber somewhat, but a longer exposure at a lower temperature gave equally good results. As the resulting solution showed a tendency to gelatinise, water was added to it, taking care not to allow it to touch the heated sides of the bottle. The refractory nature of the rock may be judged from the fact that it contained over 7 per cent MgO. 14 per cent Al_2O_3, and considerable amounts of titanium and chromium, which have not yet been determined. By using ammonium salts in the subsequent operations, they can be expelled by nitric acid, and potash and soda, if present in the mineral, can be determined.

If a pressure bottle is not at hand, one can easily be improvised. The writer found an old bromine bottle sufficiently strong.—*Journal of Analytical and Applied Chemistry*, v., No. 11.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

December 18th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. R. W. MOND, F.R.S.E., was elected a Member of the Society.

The PRESIDENT announced that it had been found necessary to alter the dates of the meetings to be held after Christmas from those already published to the following:—Jan. 22, Feb. 12 and 26, March 11 and 25, April 8, May 13 and 27, June 10 and 24.

A "*Note on Interference with Alternating Currents*" was communicated by Mr. M. H. KILGOUR. Whilst studying Dr. Fleming's paper on "Some Effects of Alternate Current Flow in Circuits having Capacity and Self-Induction," the author constructed some additional curves. He was thereby led to investigate whether the serious rises of pressure produced by adding capacity would occur over considerable ranges of capacity, or whether they would only take place when the capacity was nearly equal to a particular value. Taking the case of a condenser of capacity C farads, in series with a circuit of resistance R ohms and inductance L henrys, he showed that the maximum value of λ (the ratio of the pressure across the condenser terminals to that across the condenser and inductive resistance) is obtained when $C = \frac{L}{R^2 + p^2 L^2}$ (1), where $p = 2\pi$ times the frequency. The maximum of λ produced by this capacity being given by the expression—

$$\Lambda = \frac{\sqrt{R^2 + p^2 L^2}}{R} \quad (2).$$

Taking R = 10 and $p = 2\pi \cdot 1000$, curves plotted from equations (1) and (2) between C and L, and between Λ and L, had been drawn. The C L curve rises to a very sharp peak at L = 0·0015, and falls rapidly. That between Λ and L starts horizontal and bends upwards, and approximates to an inclined straight line for values of L greater than 0·002; when L = 0·1, Λ = 63.

Considering the question of the range of capacity with which a given rise of pressure can occur, it was pointed out that when the value of L, R, and p are such as to make a large rise possible, a rise exceeding a moderate value can only be obtained for values of C differing little from that given by equation (1). On the other hand, when the circuit is such that the maximum rise possible is not large, then a rise exceeding a given moderate value can be obtained over a much wider range of capacity. Hence the author concludes that the larger the possible rise, the smaller is the probability of a serious rise occurring.

The effect of shunting the condenser by a circuit of resistance r and inductance l is next dealt with in the paper, and the values of C which make λ a maximum determined, as well as the maximum value λ can have.

Subsequently the author examines whether the practical

case of an alternator feeding a transformer through a concentric cable may be simplified without introducing serious error, by assuming the capacity concentrated at either end of the cable, and concludes that in ordinary cases little error will be thus made. In an experiment made with a 100 kilowatt alternator, $\frac{3}{8}$ mile of $\frac{1}{11}$ concentric cable, and an 18 kilowatt transformer, a rise $\frac{1}{4}$ per cent was found to occur at the terminals of the alternator when the cable was connected. Putting on the transformer unloaded or loaded produced little change in the rise of pressure, this in all cases being between 0·2 and 0·3 per cent.

Dr. Sumpner asked whether the conclusions as to the range of capacity with which a given rise of pressure was possible was true for small rises such as occur in practice. Cases where the maximum possible rise was of the order 63 were not likely to occur at ordinary frequencies. The highest rise he had ever known was 11. He thought the time λ constant of the inductive coil chosen, viz., $\frac{1}{150}$ of a second, was very large. In circuits containing iron it was practically impossible to get such large time constants, for the power spent in the iron increased the effective resistance. Referring to the narrow range of capacity, within which large rises were possible, he pointed out that such cases were found in Hertz's resonators, where the rises were immense, but to obtain them the adjustments had to be very accurately made.

Dr. S. P. Thompson said he regretted that Professor Fleming was not present, for he had recently investigated Hertz's experiments and had obtained curves very similar to those got for the Deptford mains.

The curve between λ and L was very interesting. It was, in fact, a curve between the secant of the angle of lag and L, as could be seen from formula (2). In practice one would be working on the lower portion, and hence the rises would be small.

Mr. Kilgour explained that in the paper his first object was to show that the product of the range of capacity between which a rise greater than a given value would occur, and the maximum possible rise, was approximately constant for different circuits. Secondly, he wished to prove that the capacity of concentric cables could be assumed to be localised at either end without introducing much error in the rises of pressure calculated therefrom.

Dr. Thompson, speaking of nomenclature, regretted that the word inductance should be used sometimes for L, and at other times for $L\rho$, and thought its meaning should be restricted to the latter.

Prof. Perry said a name was needed for co-efficient of self induction. Resistance was practically independent of frequency, and "inductance" should have no reference to frequency.

Dr. Sumpner thought it important to have a name for $L\rho$, for that quantity comes into calculations most frequently. He would have preferred that "inductance" should mean $L\rho$, but Mr. O. Heaviside, who introduced the term, had used it for L.

The President remarked that some time ago Dr. Sumpner and himself felt the need of a name for $L\rho$, and thought of using "inductance," but on referring to Mr. Heaviside's articles found it used for L.

Dr. C. V. Burton asked whether the word "self-induction" could not be used as an abbreviation for "co-efficient of self-induction."

Dr. Thompson pointed out that this word already had a meaning, viz., L multiplied by current.

Dr. Burton then suggested that inductivity might be applicable.

Dr. Thompson said the word "impedance" was also used ambiguously, for the sense in which Dr. Lodge uses it, in his "Modern Views of Electricity," is not the same as the vector sum of R and $L\rho$.

Prof. Perry recalled the fact that "impedance" had been defined by the Committee of the British Association as the ratio $\frac{\text{Effective voltage}}{\text{Effective current}}$.

Dr. Thompson said this definition was only applicable to periodic currents and not to intermittent or transient ones.

The President said he understood the first object of Mr. Kilgour's paper was to enquire whether the dread of rise of voltage occurring when concentric mains were used, need exist. When Dr. Fleming's paper was read, the general idea was that concentric cables were dangerous. In the discussion on it, he, amongst others, had pointed out that the chance of a large rise of pressure was not a serious one. Mr. Kilgour had now shown that the range of capacity over which a particular rise could occur is inversely proportional to the maximum rise possible in the particular circuit. When the circuit was such that a large rise was possible, the probability of any serious rise taking place was very small; hence, the fears of large rises were more or less unfounded.

The second part of the paper was to show that ordinary problems on concentric cables could, in practice, be treated with sufficient accuracy by assuming the capacity localised at either end of the cable, instead of being distributed its length.

NOTICES OF BOOKS.

The Metallurgy of Argentiferous Lead. A Practical Treatise on the Smelting of Silver-Lead Ores and the Refining of Lead Bullion. By M. Eisler, Mining Engineer and Metallurgical Chemist. With 183 Illustrations. Crown 8vo., pp. 396. London: Crosby Lockwood and Son.

Mr. M. Eisler's former works on the metallurgy of gold and of silver have given such general satisfaction that the present volume may be sure of a favourable reception. But it may well claim the right of standing on its own merits, which are undeniable. In his introductory chapter the author gives a general survey of the occurrence and distribution of this metal. It is very commonly accompanied by silver, and seems to have a predilection for calcareous rocks in whatever geological formation they may be found. In short, various and extensive as are the applications of lead,—in some cases deplorably so,—there is no reason to expect that the supply may fall short.

The author then discusses in succession the reduction of lead ores in reverberatories, the smelting of lead ores in blast furnaces, the construction of such furnaces, water jacket furnaces, the process of smelting, and the roasting of lead ores. Hence we encounter the same three modifications as in the case of copper ores, heap-roasting, stall-roasting, and kiln-roasting. The proportion of sulphur is so much smaller in lead ore than in iron and copper pyrites, that galena alone cannot be used to feed the chambers. Sometimes, however, the matte produced in smelting is mixed with lead ores containing foreign sulphides, when the mixture may be burnt in a kiln.

The next chapter treats of the products of the smelting operation, the crude lead being called bullion,—a name which has heretofore been restricted to the precious metals. Upon the condensation of lead fumes the author insists strongly. Unlike Mr. Peters, he holds that ores which contain antimony and arsenic "will so vitiate the atmosphere around the locality of smelting-works as to produce a most pernicious effect not only on animals but also on vegetable life." We certainly incline to his view rather than to that of Mr. Peters. At all events, when public health is concerned we should keep on the safe side, and if a doubt exists we should rather be too stringent than too lenient. The condensation of metallic and other fumes by electric action (Walker's process), is described, but Mr. Eisler does not pronounce on its efficiency.

We come next to the separation of silver by cupellation, the extraction of silver from lead, and the refining of silver-lead, and lastly to the assay of lead ores and their products. Here we find that the dry method is advocated on the same grounds which English smelters advance for retaining the Cornish assay for copper, *i.e.*, that it is a repetition on the small scale of the treatment which the ore will have to encounter in actual practice. This plea we must reject as invalid. The losses will always be found proportionally larger the smaller the scale of operations. Again, it is important for the smelter to learn how far he falls short of extracting the total metal which exists in the ore.

There is an appendix which contains, *inter alia*, the conclusions of M. Guyard (Hugo Tamm) on the smelting operations at Leadville. Here we find the statement that there are detected in the ores "traces of tin, bismuth, cobalt, indium, selenium, tellurium, and a new metal which has been imperfectly studied as yet, and which appears to lie intermediate between the metals of the iron-group and those of the lead-group."

M. Guyard finds also "that a very curious and hitherto unsuspected reaction takes place in the blast furnaces of Leadville, by means of which cobalt is completely separated from nickel (nickel being concentrated in speiss and cobalt in the skimmings of the lead pots of blast furnaces), showing that the metallurgy of both metals and their separation could be effected in lead furnaces by operating under conditions similar to those observed at Leadville."

Whoever wants to acquire a clear insight into the metallurgy of lead will do well to study this volume.

Electricity up to Date, for Light, Power, and Traction. By J. B. Verity, M.I.E.E. London and New York: Warne and Co.

This work is very fairly entitled "Electricity up to Date," and contains certain features which ought to recommend it to the general public. A very useful one is the account given of the various companies which have undertaken the supply of electric current in London for the production of light and power. How far these companies may succeed, from a commercial point of view, is a riddle which has not yet found its Œdipus. The account given of the Board of Trade regulations concerning electric lighting will also be useful. The author, in his remarks on overhead conductors, seems to speak more in the interest of the supply companies than of the public, whose interest must, of course, be accepted as paramount.

The remarks on "electric engineering as a calling" will, we hope, act in certain directions as a much needed "wet blanket." In these days there is no such thing as "an unworked lode." We read here—what we know to be the truth—that "there is at present nothing like sufficient work for the enormous number who have drifted into electrical engineering during the past four or five years through every conceivable channel."

Mr. Verity gives also little encouragement to the many who cling to the hope that electricity may some day deliver us from steam and its attending nuisances. He writes that "the dynamo affords the most economical means of producing electricity, and will probably continue so to do." But save in those exceptional cases where water-power is available, the dynamo means coal-smoke, soot, ashes, coal-mines, and coal miners, with strikes, rings, and all the other machinery of modern industrialism.

Modern American Methods of Copper Smelting. By E. D. Peters, Jun., M.E., M.D. Second edition, revised and enlarged. New York: Scientific Publishing Company.

Metallurgy seems at present to be attracting more attention than any other department of industrial chemistry. The work before us is a favourable result of this tendency. To European, Australian, and probably African miners and smelters, a thorough practical insight into what is being done in the United States will be of unquestionable value. The only drawback is that the working cost of the various processes, the outlay for labour, fuel, and all other materials consumed, are based upon American prices and general conditions, and will hence be no certain guide in other localities.

The question of the assay of copper forms the subject of an ably written chapter. Four methods are described, the volumetric process with potassium cyanide, the precipitation method with zinc or iron, the colorimetric process, which the author recognises as adapted mainly for slags and tailings, and lastly the electrolytic process, which is, justifiably enough, the author's favourite. The conditions under which the cyanide process becomes untrustworthy are laid down very clearly. The author omits the Cornish assay, though he assigns a wrong reason for so doing.

Copper ore still seems to be very extensively roasted in the open air, or otherwise without absorption and condensation of the sulphurous acid given off.

Into the injuries occasioned by such fumes we need not enter, as they were thoroughly discussed whilst the Alkali Acts were under consideration. Mr. Peters fully admits that the only safe way of dealing with pyritic copper ores is to pass the gaseous products into chambers. Still there occur materials containing too little sulphur to be usefully burnt in the kilns, though enough to occasion a decided nuisance. It is here stated that the damage to crops and forests is caused solely by sulphurous and sulphuric acids, arsenical and antimonial fumes having no appreciable influence. It may reasonably be doubted whether arsenical fumes are totally inert as regards human health, and we may also ask if crops have ever been fully and persistently exposed to the action of arsenic and antimony in the total absence of sulphur fumes. The loss of copper by roasting the ores in heaps is said to be appreciable, about 1½ per cent on the assay value of the ores being thus sacrificed. As regards the cost of ore-roasting the information given is to any non-American exceedingly vague. The author speaks of what is done with a "cord" of wood. But to those who do not know whether a "cord" is a weight or a measure this is no information at all.

Whilst describing the roasting of ore in kilns Dr. Peters protests against the use of iron monosulphide. "It seems scarcely credible that extensive works for the manufacture of sulphuric acid and copper should have been erected, their ore supply being entirely derived from a deposit of the valueless monosulphide."

Ores in the condition known in Britain as "smalls" are in this work called "fines." The application of the Bessemer process to copper mattes is described in the last chapter. The process is pronounced as technically successful, but as useful only under certain conditions. The author's opinion is that the basic lining under present conditions would be of little use in the United States. The reason is that all arsenical or antimonial matte there produced is rich enough in the precious metals to warrant their extraction, during which operation the arsenic is eliminated.

It is interesting to learn that buyers often judge of coppers not by chemical or physical tests but by colour, a rose shade being accepted as the sign of a superior quality. Hence "dippings" have been devised for giving inferior samples this desired colour!

Metallurgists, and in general all persons interested in the copper trade, will find it advantageous to add this book to their library of reference.

Detection of Paraphenetidine in Phenacetine.—L. Reuter.—The author finds the reaction of the poisonous paraphenetidine with solution of iodine as less sensitive than that with chloral hydrate.—*Zeit. Anal. Chem.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiii., No. 24, December 14.

The Fixation of Nitrogen by Arable Soil.—Arm. Gautier and R. Drouin.—The authors, whilst admitting that atmospheric nitrogen is fixed, according to the researches of Th. Schloesing, jun., and E. Laurent (*Comptes Rendus*, vol. cxiii., p. 776), by the action of inferior green vegetation, especially chlorophyllic algæ, conclude from their previous experiments that the soil itself takes part in the process (see *Comptes Rendus*, vol. cxi., pp. 1174, 1233, and 1234). They argue that a small quantity of combined nitrogen is produced in the soil itself in virtue of its porosity, of its oxidisable organic matter, and of the aërobic microbia which provoke this oxidation. The preparatory absorption of the nitrogen by the microbia is doubtless one of the conditions of its oxidation. These organisms then give it up to the soil in the state of organic and amidic nitrogen. The algæ, the nitric and nitrous ferments, intervene in turn to fix these residues, but their intervention does not appear indispensable, as it is shown by the author's experiments, those especially in which neither algæ nor nitric ferments were present. By reducing the ammonia of the soil almost to nul, these latter organisms reproduce the conditions favourable to the action of the microbia which oxidise the humic matter and fix the nitrogen. Thus is explained at once the part of the humic matter, the utility of the ventilation and the cultivation of the soil, the non-assimilation of nitrogen in soils sterilised by heat or by antiseptics, as was observed long ago by M. Berthelot, and the influence of the superficial algæ. The soils containing organic matter, and such only, fix the free or the ammoniacal nitrogen of the atmosphere, even in the absence of plants, and the organic matter which exists in every arable soil is the indispensable medium for the formation of nitrogen.

Camphoric and Isocamphoric Ethers, and on the Constitution of the Camphoric Acids.—C. Friedel.—This lengthy paper is not adapted for useful abstraction.

Remarks on the History of Supersaturation.—Lecoq de Boisbaudran.—The author considers that supersaturation is a fact which is absolutely general, which is indispensable to crystallisation, and which accompanies all changes of state.

Three Basicities of Phosphoric Acid.—Daniel Berthelot.—Phosphoric acid is not a true tribasic acid, but rather a monobasic acid with complex functions. Its first function reminds us of that of the strong acids, its second of that of the weak acids, and its third that of phenol.

The State of Salts in Solutions: Sodium Sulphate and Strontium Chloride.—A. Etard.—The author has recently verified the conclusion that between 235° and 320° sodium sulphate follows a line of solubility which rapidly decreases, as it is shown graphically.

On a Green Solid Chromium Sesquisulphate.—A. Recoura.—The author finds that either on producing chromium sulphate in presence of a very small quantity of water, or by partially dehydrating by heat the crystalline violet sulphate, we obtain a new variety of chromium sulphate which is green, sold, and crystalline. It possesses properties quite distinct from those of the violet sulphate. M. Etard has also shown that if the solid violet sulphate is placed in contact with dehydrating liquids such as SO_4H_2 or NO_3H, it becomes green. But this is only a transient modification, for when the green sulphate thus obtained is freed from the dehydrating liquid it quickly returns to the violet condition.

On Bismuthic Acid.—G. André.—The author has formed and examined potassium bismuthate, and concludes that it is exceedingly difficult to obtain a bismuthic acid of constant composition. The combination of potassium with bismuthic acid is never complete and does not allow us to reach the composition of a neutral salt.

The Distillation of Coal.—Pierre Martin.—The author, at the instigation of the Société d'Encouragement, has executed analytical and calorimetric researches on fuels. In the present paper he gives his results with the coal of Commentry.

A Novel Porcelain: Asbestos Porcelain.—F. Garros.—The author has obtained a novel porcelain by grinding asbestos to an impalpable powder, removing iron, &c., if necessary, by treatment with hydrochloric acid, making the powder into a paste with water, and baking it in a porcelain furnace for 18 hours at 1200°. The porcelain thus produced may be used for the filtration and sterilisation of liquids. The experiments of Drs. Durand-Fardel and Bordas have proved that water containing 1200 colonies of microbes per c.c. are absolutely sterile after filtration through asbestos porcelain. At the same time it filters more rapidly than ordinary porcelain. Other comparative experiments made with the co-operation of MM. Cousin and Méran on the filtration of wines, vinegars, and acids, show that the porcelain may serve equally for the filtration and sterilisation of wines, vinegars, &c., and for the filtration of acids. (This invention must open out a new prospect for the asbestos districts of Canada).

Zeitschrift fur Analytische Chemie. Vol. xxx., Part 4.

A Method for Conducting Elementary Analyses Electrothermically.—Johann Oser (*Kaiser. Akademie der Wissensch. in Wein. Math. Naturwissen. Classe*).—This paper does not admit of useful abstraction.

Method for the Volumetric Determination of Chloroform.—L. de Saint Martin.—(From *Comptes Rendus*, vol. cvi., p. 492).

Lead and its Sophistications.—H. W. Wiley.—(From "Foods and Food Adulterants,"—an investigation made by the Commissioners of Agriculture of the United States).

Geranium Oil.—Schimmel and Co.—This product is now largely sophisticated with fatty oils. This fraud can be detected by the behaviour of the sample with dilute alcohol. Pure geranium oil dissolves in 2—3 vols. of alcohol of 70 per cent (by volume) at 20°. If small quantities of fat are present the mixture is dull, or in case of larger quantities milky.

Detection of Chlorinised Compounds in Oil of Bitter Almonds.—Schimmel and Co.—The process given by the authors in *Zeit.* (vol. xxx., p. 90), is contested by Merck.

Impurity in the Pure Benzol of Commerce.—C. Liebermann and A. Seyenitz.—These authors (*Berichte Deuts. Chem. Gesell.*) state that this article contains considerable quantities of carbon disulphite, which appears to be a constant associate of coal-tar benzol. For its detection the authors add to 10 c.c. of benzol 4—5 drops of phenylhydrazine, and let the mixture stand from 60—90 minutes with frequent shaking. In presence of 0·2 per cent carbon disulphide there is formed a precipitate of phenylhydrazine phenylsulphocarbazinate which renders the liquid quite thick. The limit of the reaction is reached at 0·02 per cent (0·17 grm. per litre).

On Volumetric Determination of Hydrocarbon Vapours in Coal-Gas.—W. Hempel and L. M. Dennis (*Berichte Deuts. Chem. Gesell.*).—Already inserted.

Determinations of the Penta-Glycoses in Plants.—A. Günther and B. Tollens (*Ber. Deuts. Chem. Gesell.*).

—The author has operated on cherry-gum, wheat and oat straw, beech, and pine-wood. The first-mentioned material contains 45—46 per cent of arabinose.

Determination of the Specific Gravity of Blood, Alkapton Urine, Uroleucic Acid, Indigo Red in Urine, Hæmatoporphyrine.—For the detection of bile pigments in urine, and melanogenous substances in urine, we must refer to the original.

Detection of Mercury in Chemico-Judicial Investigations.—T. Lecco (*Berichte*).—The author shows that mercury is very sparingly soluble in hydrochloric acid and potassium chlorate, so that the reaction must be continued for hours after the organic substance is destroyed, applying heat and stirring.

Detection of Phosphorus Poisoning.—Th. Poleck.—Phosphorus acid was found by Blondlot's method three months after the death of the subject.

Detection of Cyanogen Compounds.—A. Hilger and K. Tamba.—The authors reject the use of the well-known copper sulphate and guiacum papers. The substances are first mixed with tartaric acid, gradually rendered slightly alkaline with sodium carbonate, and then treated for some time at 60° (not higher) in a current of carbonic acid in a distillatory apparatus. The distillate is tested with the usual reagents for hydrocyanic acid.

Re-determination of the Atomic Weight of Glucinum. — Gerhard Kruss and H. Moraht. — The atomic weight (O = 15·96), appears to be 9·027, and the equivalent 4·5134.

Vol. xxx., Part 5.

Statistics of Wine-Production in Germany.—No. IV.—An elaborate report having no direct connection with analytical chemistry.

Contributions to the Characteristics of the Alkaline Earths and of Zinc Oxide.—Dr. G. Brugelmann.—The author originally used graphite crucibles for the preparation of baryta from barium hydroxide, as he expected that vessels of clay, porcelain, and platinum would be too strongly attacked. But even in crucibles of graphite it is impossible to obtain pure baryta from the hydrate, since, in addition to the ash of the fuel, they contain admixtures of clay, sand, &c. By the great rapidity of the decomposition, the absorption by the melting hydrate of material from the crucibles was much restricted, but not obviated. The "needles" in question were found not to be pure BaO, but a compound of this oxide with the materials of the crucible. They do not form a clear solution in water, but leave a considerable residue. The author has not examined whether this is a compound of baryta with alumina or silica, or both, or perhaps with other constituents of the crucible. What has just been said applies, though to a less extent, to the production of strontia and lime. Hence, whatever the author has formerly stated on the preparation of the alkaline earthy oxides from their hydrates and carbonates in other than platinum vessels must be deleted as non-valid, as also the figures given for the specific weight, the acicular form of baryta, the dimorphism of this oxide, and the suggested catalytic action of platinum. The author cannot confirm the assertion that strontium carbonate melts during its decomposition; it is merely fritted to a slight extent. The rapid and complete dehydration of barium hydroxide is effected only in the strongest white heat.

Support for Washing, Drying, and Absorbing-Tubes.—A. Gawalowski.—This paper requires the five accompanying cuts.

Separation of Baryta from Lime.—Professor R. Fresenius.—The author gives here a brief conspectus of the methods which he has discussed. 1. Complete separation of the two bases with perfectly satisfactory results: (*a*) separation by ammonium chromate with double precipitation; (*b*) separation by hydrofluosilicic acid, combined method. 2. Separation not quite perfect, but results still satisfactory: (*a*) separation by ammonium chromate, single precipitation; (*b*) separation by hydrofluosilicic acid, elutriation process. 3. Separation still less complete, but satisfactory for moderate demands; results often apparently good from the mutual compensation of opposite errors: (*a*) separation by hydrofluosilicic acid, process hitherto general; (*b*) separation of the sulphates in mechanical admixture by sodium thiosulphate; (*c*) separation by sulphuric acid in a solution strongly acidified with hydrochloric acid; (*d*) separation by heating the sulphates with potassium carbonate; (*f*) separation by precipitation with a mixture of potassium carbonate and sulphate (Fleischer); (*g*) precipitation with ammonium sulphate and oxalate, and volumetric determination of the calcium oxalate. 4. Methods which must be pronounced as scarcely useful or quite worthless: (*a*) precipitation with sulphuric acid from a solution containing little hydrochloric acid; (*b*) separation of the mixed precipitate of sulphates by sodium thiosulphates; (*c*) separation by treating sulphates with ammonium carbonate; (*d*) separation by precipitation and digestion with a concentrated solution of ammonium sulphate.

Change of Volume on Mixing two Liquids, and its Influence on Refractive Power.—L. Buchkremer.—An Inaugural Dissertation. No particulars are given.

On Jamin's Interferential Refractor.—L. H. Siertsema.—An Inaugural Dissertation; no particulars.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Gas Compression.—A correspondent wishes to know of the address of a maker of apparatus for gas compression.

MEETINGS FOR THE WEEK.

Monday, 4th.—Medical, 8.30.
Tuesday, 5th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.
—— Pathological, 8.30.
Wednesday, 6th.—Geological, 8.
Thursday, 7th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.
Friday, 8th.—Astronomical, 8.
Saturday, 9th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

Erratum.—P. 319, col. 2, line 36 from top, *for* "grammatical" *read* "gravimetrical."

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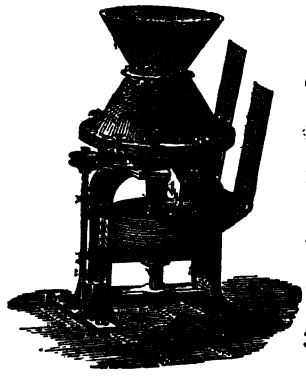

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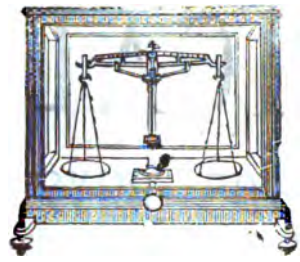

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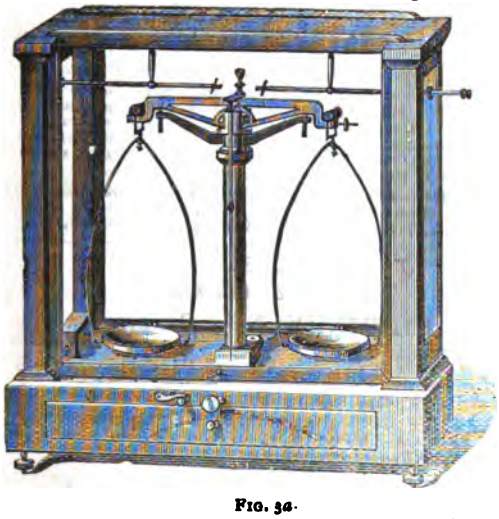

FIG. 32.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1676.

THE DENSITY OF SULPHURIC ACID SOLUTION.

By G. LUNGE.

In the Chemical News (vol. lxiv., p. 311) Prof. Pickering replies to my remarks on the relative accuracy of his and my specific gravity determinations of sulphuric acid. Those remarks had been called forth by a paper (*Journ. Soc. Chem. Ind.*, 1890, p. 479), in which Mr. H. D. Richmond — after comparing some of Prof. Pickering's figures with those formerly obtained by Naef and myself, by Winkler and by Archbutt—came to the conclusion that Prof. Pickering's determinations were preferable to all others. From these he has constructed a specific gravity table for sulphuric acid, which he gives to the world as the most accurate in existence, and as such Mr. Richmond's table has been reprinted in other publications. As I had previously published a very elaborate table of the same kind, based on the work of myself and my collaborators Naef and Isler; as I, rightly or wrongly, believed, and still believe, that *our* estimations are the most accurate hitherto made; as I, moreover, felt constrained to give my reason why I did not accept Mr. Richmond's table for the new edition of the "Alkali Makers' Pocket-Book," which was then in course of preparation, I felt bound to show why Prof. Pickering's results, in spite of the "seemingly stupendous accuracy of his observations," were not to be preferred to mine.

I do not know what more legitimate reasons for exercising criticism could have existed than those which I have stated. Prof. Pickering, however, sees fit to call this "feeling hurt, apparently, that anyone else's determinations should have been preferred to my own." It is useless to discuss the good taste of this imputation, as it is only a trifle in comparison with what follows. "Gross misrepresentations," "bold statements," "blunders made by critics who decline to read the papers which they attempt to criticise," "self-restraint on my part not to accuse the critic of a wilful misrepresentation of statements and a perversion of the facts of the case," "misrepresentations so glaring that it seems scarcely possible to attribute them to mere carelessness on his part," "ridiculous,"—these are some of the words thrown at my head. Prof. Pickering is not content with rectifying any misunderstanding which I may have commited, but he charges me with uttering deliberate falsehoods in order to calumniate him. That he covers this charge with an extremely transparent veil, barely sufficient to avoid the risk of an action for libel, I disdain to notice. But I disdain just as much to answer such a charge, which cannot but rebound upon him who has made it. Prof. Pickering does not even give me the traditional choice between knave and fool; I must needs be both in an egregious degree. He represents me as committing the incredible stupidity of wilfully calumniating him in one of the most widely circulating English chemical journals, and in a book which I must desire to be read by as many chemists as possible, with the absolute certainty of immediately encountering the phials of his wrath. I have now been before the chemical public as an author and leader for thirty-two years, and I am personally known to most of the leading English chemists; I leave it confidently to them to judge whether Prof. Pickering's accusations against me, of wilful mis-statements, is within the range of possibility or not, and I shall confine myself to answer him as if he had merely charged me with misunderstanding him. I believe that I have done so in minor points, and that I am right in the principal issue.

Prof. Pickering seems to have forgotten that hard words do not amount to *arguments*, and are generally held to show that he who uses them in a violent manner feels touched in a sore part. If I wished to use the same weapons as my antagonist, I should perhaps say that he expected extremely few of your readers would wade through the dreary wilderness of figures in his paper on Sulphuric Acid, in order to control his corrections of my alleged misrepresentations. I will not, however, follow him in the way of imputations, and merely state *facts*.

Professor Pickering implies that I ought to have taken notice of his reply to Mr. Sidney Lupton's strictures on his paper; and yet he must know that my remarks were in print many months before the controversy happened between himself and Mr. Lupton and other adversaries.

The principal point at issue between us (for I shall certainly not waste your space over the other accusations of "carelessness," which are trifles to anybody else, and are in no case of any importance at the place where they stand) is this: that I am accused of having imputed to Prof. Pickering to have claimed that the percentages of his acids are accurately known to the third decimal per cent, whilst the analyses of his acids made by Mr. Compton varied between 99·704 and 99·962 per cent. Prof. Pickering maintains that he did not rely on Mr. Compton's analyses for determining the strengths of his acids, but that he found and accepted a method more reliable than any analysis, based on the fact that the pure acid must have a higher freezing-point than any acid with excess of either water or anhydride. But in his paper, after having given Mr. Compton's analyses, and the mean value he deduces from them, and then, having mentioned his own new method, he continues (p. 73, line 5 to 10): "As all the present results had been calculated out long before this later work had afforded this more certain means of ascertaining the strength of the acid, and as the error would not appreciably affect these results when differentiated, I did not think it worth while to alter them, except in a few cases where the introduction of the correction will be specially mentioned." If that does not mean that all his results (excepting those "few cases") *were* based upon Mr. Compton's analyses, then I do not understand the meaning of English words.

On the same page Prof. Pickering describes his methods for diluting the strong acid. Employing quantities of 100 to 200 grms., and using a balance reading to 0·0001 grm., he maintains that their relative composition is accurately known to "about one unit in the fourth decimal place of the percentage." If a magnitude is known to "about one unit" of the fourth decimal, it is *accurate* to the third decimal, as I put it, and I fail to see in this case either carelessness or misrepresentation on my part. Now it is true that Prof. Pickering here uses the expression "relative composition," and I am so far in fault that I omitted to notice the word "relative." But I would defy most readers, wading through Prof. Pickering's 124 pages, and tens of thousands of figures, to bear it always in mind that all those figures refer, not to real percentages, but to "relative compositions." So much is certain, that Mr. Richmond does not mention this either, but takes Prof. Pickering's tables as representing *absolute* values; on any other basis his calculating therefrom another table for practical use would have been absurd and directly misleading. But he had evidently, like myself, taken the values as absolutely given. If Prof. Pickering claims for them only a *relative* accuracy, for differentiating purposes; they are useless for constructing practically workable tables, and I will not start a new dispute by pointing out that the limit of accuracy of the balance is far from exhausting the possible sources of error in such determinations, not even when adding his *contradicto in adjecto*, "provided no loss of anhydride occurred in making them" (the dilute acids).

Whether Prof. Pickering's new physical method for estimating the strength of sulphuric acid is really, as he believes, superior to any analytical method, I will not

stop to discuss. But I may be allowed to submit that, in my humble opinion, the great majority of chemists will, for all practical purposes, prefer a specific gravity table founded upon a basis which they all understand and can check for themselves, namely, the most accurate analytical method known, to a table founded upon the hypothetical basis that the pure hydrate must have the lowest freezing point, and adding water to this. Nor will, probably, the differentiation of the contractions by Prof. Pickering be very convincing to most people. So long as there exists such great uncertainty about the nature and properties of solutions and the hydrates contained therein, any mere paper work, founded upon differentiations of contractions, confers no right of saddling a practical observer with the blame of inaccuracy. Before such a blame can be held to be substantiated, evidence more directly appealing to chemists must come forward.

It is, perhaps, no matter of surprise that the various strong attacks made upon his laborious work on solutions have put Prof. Pickering out of temper. That does not, however, entitle him to neglect, in scientific controversy, all ordinary rules, not merely of courtesy, but of common fairness. I think I shall hence be held justified if I decline any further discussion with an antagonist who "hits below the belt."

THE CONTRACTION ON MIXING SULPHURIC ACID AND WATER.

By SPENCER U. PICKERING, F.R.S.

In a communication on the densities of sulphuric acid solutions (Chemical News, vol. lxiv., p. 312), there appeared a sentence which I had erased in the proof, but which was accidentally allowed to remain in the text: it was to the effect that it had been known for some time that the maximum contraction occurring when the acid is mixed with water is situated at different strengths according to the temperature. This statement referred to the contraction calculated per unit weight of the solution formed, and rested on the authority of Mendeleeff, who had not any very complete sets of determinations at his disposal when he deduced this conclusion (*Ber. Deut. Chem. Gesell.*, 1886, p. 387), and, on second thoughts, I considered it advisable not to repeat it before I had ascertained whether my own determinations (*Chem. Soc. Trans.*, 1890, pp. 139—144) led to similar results. These determinations I have now examined, and find that they do show the point of maximum contraction per unit weight to shift with the temperature, but that the point of maximum contraction per unit volume of solution formed is practically unaltered by temperature. This statement refers to a range of temperature from 8°—38°.

The following table contains the results. All the percentages have been corrected in accordance with the later and more accurate determinations of the strength of the acid used by me (*vide loc. cit.*, p. 73), and a very small correction has been applied to the densities at 17·925°, to correct for the error mentioned on page 72 of my communication.

On plotting out the values for the contractions per unit weight, and drawing a smoothed curve through them, the following are found to be the positions of the maximum:

At 38·203°	it is at	70·1	per cent, and =	0·059907
,, 28·064°	,,	69·1	,, ,,	0·061040
,, 17·925°	,,	67·5	,, ,,	0·061825
,, 7·978°	,,	67·0	,, ,,	0·062827

These values show an undoubted shifting of the maximum towards the stronger solutions as the temperature rises, but whether this shifting occurs at a regular rate or not cannot well be determined owing to the gradual manner in which the maximum is reached, and the consequent difficulty in determining its exact position.

The values for the maximum per unit volume are as follows:—

At 38·203°	max. at	76·3	per cent, and =	0·097957
,, 28·064°	,,	76·0	,, ,,	0·100010
,, 17·925°	,,	76·0	,, ,,	0·101585
,, 7·978°	,,	75·8	,, ,,	0·103595

A slight shifting in the same direction is shown by these numbers, but as it is considerably within the limits of experimental error this maximum must be said to be practically unaltered in position.

It will be noticed that the position of neither of these maxima agree with the composition of the dihydrate, which contains 73·14 per cent of acid, nor with any of

Contraction on Mixing Sulphuric Acid with Water at 38·203°.

Acid p.c.	Density.	Volume.	Volume of components.	Contract. per grm.	Contract. per c.c.
100	1·813643	0·551376	—	—	—
79·9112	1·707359	0·585700	0·642390	0·056690	0·096790
78·9338	1·696495	0·589451	0·646816	0·057365	0·097320
77·8920	1·684849	0·593525	0·651537	0·058012	0·097742
75·8532	1·661610	0·601826	0·660773	0·058947	0·097947
73·9337	1·639397	0·609981	0·669461	0·059480	0·097511
71·9710	1·616740	0·618529	0·678352	0·059823	0·096718
69·8816	1·592543	0·627927	0·687829	0·059902	0·095397
67·9601	1·570547	0·636719	0·696534	0·059315	0·093942
65·9782	1·548091	0·645958	0·705512	0·059554	0·092195
63·9998	1·525956	0·655327	0·714476	0·059149	0·090256
0	0·993070	1·006978	—	—	—

At 28·064°.

100	1·823805	0·548304	—	—	—
79·9112	1·717424	0·582268	0·639780	0·057512	0·098773
78·9338	1·706389	0·586033	0·644230	0·058197	0·099307
77·8920	1·694596	0·590111	0·648974	0·058863	0·099749
75·8532	1·671094	0·598411	0·658258	0·059847	0·100010
73·9337	1·648712	0·606534	0·666999	0·060465	0·099689
71·9710	1·625844	0·615065	0·675926	0·060861	0·098951
69·8816	1·601468	0·624428	0·685450	0·061022	0·097725
67·9601	1·579326	0·633182	0·694200	0·061018	0·096367
65·9782	1·556737	0·642369	0·703225	0·060856	0·094737
63·9998	1·534480	0·651687	0·712227	0·060540	0·092897
0	0·996353	1·003660	—	—	—

At 17·925°.

100	1·833937	0·545275	—	—	—
79·9279	1·727959	0·578717	0·636806	0·058089	0·100380
78·9338	1·716617	0·582541	0·641340	0·058799	0·100936
78·1989	1·708215	0·585407	0·644691	0·059284	0·101270
75·9030	1·681394	0·594745	0·655161	0·060416	0·101583
73·9517	1·658444	0·602974	0·664059	0·061085	0·101306
71·9714	1·635125	0·611574	0·673089	0·061515	0·100585
70·0480	1·612588	0·620121	0·681850	0·061729	0·099544
68·0530	1·589441	0·629152	0·690958	0·061806	0·098237
66·0860	1·566869	0·638215	0·699927	0·061712	0·096695
64·8448	1·552820	0·643990	0·705588	0·061598	0·095651
64·0663	1·543990	0·647673	0·709137	0·061464	0·094900
0	0·998712	1·001293	—	—	—

At 7·978°.

100	1·844263	0·542222	—	—	—
79·9112	1·738076	0·575349	0·634206	0·058857	0·102298
78·9338	1·726694	0·579142	0·638681	0·059539	0·102806
77·8920	1·714570	0·583237	0·643452	0·060215	0·103243
75·8532	1·690580	0·591512	0·652788	0·061276	0·103592
73·9337	1·667782	0·599599	0·661577	0·061978	0·103366
71·9710	1·644541	0·608072	0·670554	0·062482	0·102754
69·8816	1·619860	0·617352	0·680130	0·062778	0·101713
67·9601	1·597410	0·626013	0·688929	0·062916	0·100503
65·9782	1·574588	0·635087	0·698003	0·062916	0·099067
63·9998	1·552015	0·644324	0·707063	0·062739	0·097372
0	0·999890	1·000110	—	—	—

the hydrates the existence of which I inferred from breaks in the curves representing various properties of the solutions, and it is scarcely necessary for me to point out again that a maximum point by no means necessarily coincides with a change of curvature. Prof. Lunge's statement that the maximum does coincide with the dihydrate, and also Mendeleeff's statement to the same effect ("Principles of Chemistry," vol. ii., 237), cannot, therefore, be accepted as correct.

An interesting point may be noticed respecting the contraction, namely, that the effect of temperature upon its value does not vary in any very simple or apparently regular manner with the temperature. Thus, taking the amount of contraction per unit volume occurring at the maximum (76 per cent), this amount increases at the rate of 0·000203 per degree from 38°—28°, at the rate of 0·000155 from 28°—18°, and at the rate of 0·000202 from 18°—8°, the rate for both the extreme temperature intervals being much greater than that for the intermediate interval. The irregularity is far too great to be attributed to any experimental error, for it would require errors twenty or thirty times greater than the known experimental errors, to reduce these three rates so as to bear any simple relation to the actual temperatures, and, moreover, the seeming irregularity occurs not only with solutions of one particular strength, but throughout the whole range over which the present calculations extend: thus with 64 and 80 per cent solutions the following rates of increase of contraction occur:—

	64 per cent.	80 per cent.
38°—28°	0·000260 per deg.	0·000193 per deg.
28°—18°	0·000191 ,,	0·000161 ,,
18°—8°	0·000254 ,,	0·000194 ,,

ON THE ACTION OF HEAT ON SOLUTIONS OF SALTS OF CHROMIUM.

By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

It has long been known that there are two kinds of chromium salts capable of existing in solutions, namely the red, violet, or blue, and the green modifications. The difference in constitution between the green and the other salts of chromium was in part the subject of researches made by me in the year 1872-74. A preliminary notice was published in the *Proceedings* of the Royal Society, vol. xxii., p. 241; and a full account of the work was submitted to the Royal Society at a later date, together with a brief extract, entitled, "On the Action of Heat on the Absorption Spectra and Chemical Constitution of Saline Solutions." This appeared in the *Proceedings*, vol. xxxiii., p. 372, 1875.

It contains the following paragraph:—"The action of heat on the violet hydrated compounds of chromium is not simply a dissociation of water molecules, or of acid from base, but a true decomposition, resulting in the production of a different class of salts with different generic properties.

The publication of the paper in full was postponed for the completion of certain physical measurements which would have increased its interest, but, owing to the fact that at the time it became impossible to execute this additional work, the entire paper has never been printed.

The general conclusions derived from the spectroscopic examination and determination of the chemical constitution of a large number of salts, some of which were rare and others entirely new, were in no way affected by the omission of the details to which I refer.

The most complete, though still inadequate, record of this work is contained in the *Proceedings* of the Royal Institution, for 1875, being the report of a Friday evening discourse delivered on April 30th, to a portion of which additional interest is lent at the present time on account of a recent thermo-chemical investigation of M. A. Recoura, on the action of heat on solutions of chromic oxide (*Comptes Rendus*, cxii., p. 1439.

It was shown that green solutions of chromium, having the same absorption spectrum, may be produced from the sulphate or nitrate by the three following methods:—(1) By boiling a solution of the purple salt; (2) By dissolving an excess of the bluish chromic hydrate in the purple solution; (3) By neutralising with an alkali one-third of the acid in a solution of the purple salts.

If 50 c.c. of a solution of the sulphate or nitrate be boiled so as to form the green salt, it will not yield a precipitate if diluted with two or three litres of water and further boiled; but when one-third of the acid present has been previously neutralised, or when an excess of chromic hydrate is dissolved in the blue solution, a basic salt is thrown down on boiling with much water. This is exactly the behaviour characteristic of a salt described by Schrötter, to which he assigned the formula $Cr_2O_3.2SO_3$, which may be written $Cr_2O.2SO_4$. Lœwel has described a chloride, which is formed at 100° C.; this he formulates thus:—$Cr_2O_3.4HCl$, and the formula may be modified in the following manner, $Cr_2O.Cl_4.2H_2O$. The constitution thus modified has the recommendation that it explains the decomposition of the substance when heated to a high temperature, which Lœwel's formula does not. At or about 300° C. the compound is resolved into a mixture of the anhydrous violet chloride, $CrCl_3$ or Cr_2Cl_6, and the anhydrous green oxide, Cr_2O_3. If the original salt were merely a combination of the chromic oxide with hydrochloric acid, heating would drive off the volatile acid and leave the oxide only, but the actual change indicates that the chromium and chlorine are in direct combination.

Hence the conclusion that the effect of heat on the purple chromium solutions is not traceable to dehydration, but to a well-defined chemical reaction which yields a distinct class of compounds.

The violet or purple compounds of chromium have the general formula $Cr'''R_3.xH_2O$, or $Cr'''_2R''_3.xH_2O$, where R is Cl or NO_3 and R'' is SO_4, or the like.

When solutions of these are heated to 100° C. there is formed a class of substances which may be written thus: $Cr'''_2OR_4.xH_2O$, and $Cr'''_2OR''_2xH_2O$, or the first compounds may be said to contain Cr''' as the base, while the second contains the radical Cr'''_2O. This tetrad radicle I proposed to term *chromyl*, just as UrO is called uranyl.

The conclusions of M. Recoura are to the effect that when a purple solution of chromium sulphate has been converted into the green modification by boiling, exactly half an equivalent of free H_2SO_4 exists for each $Cr_2O_3.3SO_3$ from which it has been derived.

It thus appears that the basic green salt formed by the action of heat on a normal solution of chromic sulphate, has the definite composition of $2Cr_2O_3.5SO_3$, and that it contains a modified form of chromic oxide which, definite experiments showed, is incapable of combining with more acid than the formula above indicates.

The following is the mode of operating in order to arrive at this conclusion. A solution of the sulphate which has been converted from the purple to the green condition by boiling is mixed with an exactly-measured quantity of soda solution, and the heat evolved is measured. If the heat evolved be in accordance with that liberated by free sulphuric acid, under the same conditions of dilution, namely 31·2 heat units for every proportion represented by Na_2O, it may be concluded that the soda has not decomposed the chromium salt, but simply neutralised an equivalent quantity of free acid.

To verify this result a quantity of sulphuric acid equivalent to the quantity of soda previously used is added to the solution. By this means it was ascertained that there was no evolution of heat, but, on the contrary, a slight heat absorption equivalent to 0·2 heat units for Na_2SO_4, which, M. Recoura mentions, is due to

the action of the free acid upon the sodium sulphate. But when an excess of soda amounting to no more than 1-20th an equivalent beyond that necessary to neutralise the free sulphuric acid was used, the subsequent addition of acid caused heat evolution, which arose from the action of the acid upon the chromium hydrate set free by the 1-20th Na_2O (+0·6 heat unit).

It is admitted that the salt $2Cr_2O_3.5SO_3$ contained in solution does not yield an oxide or hydrate capable of the same degree of saturation as that indicated in this formula, for when the base is precipitated by an alkali it combines with only two molecules of H_2SO_4, as shown by the following thermo-chemical equation:—

* Cr_2O_3 (green precipitate) + $2H_2SO_4$ (solution) = $= Cr_2O_3.2SO_3$ (solution) + 34·8 heat units.

If another molecule of acid be added, there is no further reaction, thus:—

$Cr_2O_3.2SO_3$ (solution) + H_2SO_4 (solution) = $= Cr_2O_3.2SO_3$ (solution) + H_2SO_4 − 0·8 heat unit.

As this reaction is feebly endothermic, there is evidently no further combination of the acid with base or with the basic sulphate. M. Recoura therefore concludes that the salt in solution is $2Cr_2O_3.5SO_3$, but that the salt formed by the action of sulphuric acid on the green precipitated hydrate, obtained from this solution, is $Cr_2O_3.2SO_3$. He states that "*the oxide precipitated is a new modified oxide of which one molecule fixes only two molecules of sulphuric acid.*"

Not only, therefore, are the conclusions as to the existence of this oxide and a new class of salts, as described in the *Proceedings of the Royal Institution*, confirmed, but M. Recoura's work also demonstrates the existence of two green sulphates with different compositions, as stated above, and thus affords an explanation of the difference in behaviour of dilute solutions of these salts when boiled. The empirical formulæ determined may very inadequately represent the constitution of the salts in these solutions, for they are almost certainly hydrated salts.

ON THE

DETERMINATION OF THE MELTING POINTS OF MINERALS.†

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., D.Sc., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

(Continued from p. 3).

Sublimation on the Meldometer.

ALTHOUGH the majority of mineral bodies have melting-points ranging over 900° C., some, such as the sulphides, arsenides, and some of the elements, can even be brought into the state of vapour upon the meldometer. When this is the case we find that this apparatus affords a means of obtaining sublimates much transcending the blowpipe (used either with carbon or aluminium) in delicacy, range, and purity. Sublimates may, in fact, easily be obtained from substances which treated in the blowpipe would appear to afford none, as will appear. The mode of procedure is as follows:—A circular cover-glass, not too thin, grasped in a forceps, is held horizontally above the platinum ribbon, as the temperature is being raised. If the sublimate is one which oxidises, we obtain the oxidised sublimate alone; or the unoxidised sublimate bordered by the oxide, according as we hold the glass further or nearer to the ribbon.

The more volatile elements often afford as sublimates both the element and an oxide of it. The elemental sublimate may often be obtained nearly pure by suitably regulating the temperature. Thus, at low temperatures, *arsenic* sublimes as a rich grey-black sublimate, showing the mirror when viewed through the glass. At a higher temperature, especially if the glass is held at a distance of 3 or 4 c.m. above the ribbon, the white oxide—the trioxide—only is obtained. Sometimes both element and oxide are together on the one glass, affording an "eye," the pupil of which is the element. This results from the screening action of the outer parts of the ascending column of vapour, the central parts being, in fact, sublimed in the absence of oxygen, which is all absorbed in the outer layers of the vapour. *Magnesium* affords similar eyes surrounded by the white oxide, or in many cases veiled over by it, so that the dark metal is only seen through the glass. The great avidity of this element for oxygen is shown in this fact. *Tin* also affords "eyes." *Thallium* throws a rich black velvety sublimate, fringed with deep ash-red (the oxide?). This is a very beautiful sublimate, but very fleeting, the black soon fading into a pale greyish-brown colour. If immediately enclosed from the air it retains its original tints a longer time. *Cadmium* may also be sublimed as the metal and its oxide. *Indium* affords a white sublimate, dashed with pink and yellow.

While the metal is thus sometimes obtained with the oxide, it more generally affords the oxide only. This is the case, so far as I have observed, with *vanadium*, *lead*, *wolfram*, *bismuth*, *tellurium*, *zinc*, and *antimony*. But, again, sometimes the element appears to sublime without oxidising. Thus *silver* affords a grey-black veil of the metal, iridescent where thinly deposited. *Gold* is also sublimed. *Sulphur* is another case, the oxide being a gas at atmospheric temperatures. *Mercury* gives a sublimate of a grey colour, consisting of globules of the element.

As regards compounds, the command we have over the temperature in the meldometer enables many very distinct separations to be effected. Thus, dealing with *realgar*, at low temperatures, the substance is sublimed unaltered in a rich yellow sublimate. Somewhat higher a decomposition is effected, the free arsenic showing as a white sublimate of the oxide round a yellow eye of sublimed realgar. As the temperature rises the effect is more and more that proper to arsenic only, the liberated sulphur not appearing; but the eyes remain most generally distinctly touched with realgar. *Orpiment* behaves in a similar manner. *Pyrargyrite*, a compound of silver and antimony sulphides, throws off the antimony first in a rich white sublimate of the oxide, touched more or less with a pale pink cloud, probably the unaltered compound. A bead of silver is left upon the ribbon, which ultimately volatilises to the grey-black sublimate of silver. *Clausthalite*, the selenite of lead, affords first a sublimate of selenium, a fine ash-red; this then becomes veiled over and intermixed with the rich yellow and whites of the lead oxides, so that a very beautiful marbling is produced, which shows stronger tints of red seen from the back of the glass than from the front.

Many such effects are seen in a similar order with the blowpipe, but are not produced with the ease, certainty, and cleanliness obtaining with the meldometer. Tests may very conveniently be applied to these sublimates as they repose upon the glass, in the knowledge that the only addition to the original substance can be oxygen. Sublimates also may be obtained from very minute quantities of the substance. This is an advantage in more ways than one. Many of the bodies mentioned above—as arsenic, tin, zinc, bismuth—attack the platinum ribbon

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* It may be remarked that in the above equations, where O=16, the heat units evolved are + 34·8, while for O=8 the number is of course one half or + 17·4, as in the original publication. An error occurs in the abstract of this paper in the *Journ. Soc. Chem. Ind*, vol. x., p. 925, for the symbols are written with O = 16, and the thermal values with O = 8. The liability to mistakes which arises from the conversion of equivalent into atomic formulæ would be lessened by quoting thermal equations exactly as written, whether they be additionally translated into atomic formulæ or not.

† A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

at high temperatures, and cut it if more than a very small quantity be used. The metals iron, gold, and silver again amalgamate with it. If it is desired, however, to obtain considerable quantities of the sublimates of the more volatile elements, it is possible by laying upon the ribbon a small slip of thin mica, and upon this the substance, to volatilise considerable quantities of it. Lest it be urged that this apparatus is an expensive one to use, owing to the necessity of using platinum, I may mention that a spool of the pure platinum ribbon, having a length of 1700 c.m. wound upon it, is supplied to me by Messrs. Johnson and Matthey, of Hatton Garden, London, at a cost of twenty shillings. This lasts an indefinite time, as a couple of centimetres serves most generally for many observations, and in the case of silicates may then often be cleaned, so as to be again serviceable, by treatment in acids. That the platinum, however, volatilises slowly at high temperature is shown by the fact that if fragments of quartz be heated upon it nearly to their melting-point, they will be found to become covered with minute crystals of platinum upon their upper surface (see *Nature*, xliv., 1891, p. 124).

But the meldometer is capable of affording sublimates which the blowpipe very certainly will not reveal. Thus, for example, *tourmaline* affords a pale whitish-yellow sublimate, the nature of which I have not determined; and *enstatite* volatilises at the highest temperatures obtainable, very nearly, giving a pale brown sublimate. An addition may be made to this form of the meldometer, which will permit of sublimates being obtained in the absence of free oxygen. This is an annular chamber of light brass open at both sides, and cut into at two points, so that it can be set down upon the base plate of the meldometer, the two slots admitting the forceps without making contact with them. It is provided with two small projections which, entering perforations in the base plate, retain it in position. It is shown dotted in fig. 1. Across the upper surface of this box the cover-glass to receive the sublimate is placed, and the sublimate thrown upon it in the usual manner. A tubular at one side permits of connexion with a supply of CO_2 or other gas, which, flowing in very slowly under slight pressure, and escaping around the forceps, replaces the air and stops its entry. If the sublimate is a very heavy one—that is, one which falls downward when generated—a second, smaller, cover-glass is supported above the floor of the chamber upon a little tripod twisted out of wire, so as to be just beneath the forceps. In this way sublimates of realgar and arsenic may be made to afford the unoxidised substances. As it is necessary, in order to obtain an abundant sublimate, that there should only be a slow motion of the atmosphere around the platinum, guards are arranged, attached to the base plate beneath the forceps, which close the slots provided in the ring when this is in its place. It is further well to loosely close the opening between the limbs of the forceps with a little cotton-wool. A very slow current of inert gas then effectually secures that no air enters while the sublimate is being taken. However, in the use of this arrangement, the sublimate is generally obtained deposited in patterns—often very regular—upon the glass, due to slow swirling currents within the chamber.

Pyro-Chemistry on the Meldometer.

Before passing from the subject of the secondary uses to which this form of the meldometer may be put, it remains to add that much of the pyro-chemical work done with the blowpipe may with greater ease and delicacy be effected upon the meldometer. Thus, glasses with microcosmic salt or with borax may be made readily upon the ribbon, the colours produced being well seen, and that, too, however deep in tint, where they thin out at the ends along the bright platinum strip.

Again, abandoning the use of the ribbon, we may substitute a platinum wire carrying a loop at its centre, and, clamping it in the forceps, form beads of the usual form from the action of the hot wire. These may be observed, under the microscope, while hot. Changes of colour, often so characteristic, are very distinctly observed through the microscope, directed upon the platinum ribbon. For example, the changes of tint of a glass formed of copper oxide (CuO) with borax, coating the ribbon, as the temperature is *slowly* raised, is from a fine blue through every gradation of tint to a greenish-yellow. The command we possess over the temperature enables these successive changes to be very readily observed. Similarly, the oxidising effects of the blowpipe may be obtained by addition of oxidising substances, such as potassium nitrate. Thus, as with the blowpipe, a glass formed of the sesquioxide of cerium and microcosmic salt, which is a pale yellow when hot, passing to colourless when cold, may, by the addition of KNO_3, be intensified to a vivid yellow when hot, to colourless when cold. By the use of reducing agents deoxidation may, of course, be effected. In this way a mixture of cupric oxide with carbonate of soda and cyanide of potassium yields, first the lower cuprous oxide as a transparent red crystalline body, and finally the metal which alloys with the platinum. The most minute quantities may be used. I have not had leisure to develop this application of the meldometer, but would call the attention of those versed in pyro-chemistry to the facilities it offers for minute and clean work. The form now described possesses the added advantage that the temperature at which any phenomenon is occurring can be determined with as much facility as we read a thermometer.

Measurement of Temperature on the Meldometer.

The temperature of a homogeneous conductor of constant section, heated by the passage of a current, may be considered uniform throughout; the same at the centre of section as at the surface. The difference is measured probably by hundreds of a degree only. Prof. Heinrich Streintz has calculated (*Pogg. Ann. der Phys. und Chem.*, clx., 409) the temperature difference in certain cases, and it appears that for the present purposes it is certainly unnecessary to take it into consideration.* It is allowable further to assume that a fine dust resting upon the surface of a flat conductor, such as is used in the meldometer, is very closely at the temperature of the conductor, especially when near the central line, where, surrounded by neighbouring particles, it is sheltered from draught. It is, indeed, true that for the accuracy of the measurements made on the meldometer it is not necessary to assume that the agreement in temperature should be *exact*, as will be seen, but only that the difference should be about the same from one substance to another. The point here is that the difference being in any case very small there cannot be much diversity in the temperature difference between substance and platinum from one case to another. Assuming, then, that the average temperature throughout the cross section of the wire is that of its surface, and that the finer dust resting upon this surface is nearly at its temperature, it only remains to measure the temperature of the platinum ribbon in order to determine the temperature of the substance.

First attempts in this direction were directed at determining the temperature in terms of the electrical resistance, a well-known formula of Siemens's being used to express the relation between the two.

In these experiments the ribbon used was 6 to 8 c.m. in length, and the following temperatures of slow softening were determined:—

Adularia	865° C.
Garnet, dark red ..	972 ,,
Beryl, clear green ..	882 ,,
Actinolite, dark green	971 ,,

Beryl was observed to be a very viscous body, apparently even more so than adularia. Garnet and actinolite,

* If, however, the ribbon of platinum be raised nearly to its melting-point, it will be found that signs of fusion appear first along the central line.

on the other hand, were found to melt with comparative suddenness. Diallage behaves much as actinolite. Natrolite whitens and decrepitates before fusion. The softening temperatures of these latter minerals were not determined; but, by comparison, the specimen of diallage used was found to melt at a slightly higher temperature than the actinolite. In these experiments the platinum ribbon was enclosed in a long narrow box of platinum foil provided with a lid, through a hole in which observations were made at intervals, the hole being covered between times. The softening point was sought by prolonged exposures (up to twenty minutes) of the substance in a state of fine dust to a particular temperature of the ribbon. It has been already pointed out that at much less expenditure of time, by a somewhat different procedure, the incipient softening of viscous substances may be detected.

Subsequently Mr, Callendar (*Phil. Trans. R. S.*, clxxviii., 161) compared the readings of the air-thermometer and the platinum resistance thermometer up to 600° C. However, notwithstanding the help thus afforded, the cumbersome apparatus and tedious measurements required in the case of the meldometer, in which the resistance has to be determined while a current is traversing the circuit, rendered the method inapplicable. It was accordingly abandoned after much labour had been spent upon it, and, at a later date, the present form of meldometer devised, which depends on the thermal expansion of the ribbon for the estimation of temperature. The general mode of procedure in the present method is as follows:—Using a much longer ribbon than that previously described, we determine its increase of length (by a contrivance to be described) when a salt of known high melting-point is seen to melt upon its surface, and again when two or more other substances, differing from each other in melting-point as much as possible, are melting. This is analogous to determining the fixed points on a thermometer, and assumes, as in the latter case, nothing as to the absolute coefficient of expansion of the working substance. Thus, if we read the movement of the mercury in a thermometer when we raise it from the known temperature of melting ice to the known temperature of boiling water, we may evidently, on the assumption of the uniformity of the expansion of the mercury between the two points and of the uniformity of the bore, estimate the temperature of any intermediate reading, using a system of numbering decided upon beforehand. Similarly the assumption is made in the case of the meldometer that there is uniformity of expansion over the limits of known temperature, and for some distance beyond them. In fact, in this method, we take advantage of the experimental work of past observers. Much of this, more especially that of Carnelley and Violle, is very careful. It is sufficient to determine five or six points at various intervals along the scale, and plot the extensions corresponding as ordinates along any uniformly divided line serving as a scale of temperatures. The points so determined are joined by a line which will be found very slightly curved over its lower length, in which we use the experiments of Carnelley. In the upper range—from 900° to 1500° C.—we have very careful data of Violle's, which plot as a line of slowly increasing curvature, convex to the axis of temperature, and meeting tangentially the range covered by Carnelley's experiments. To determine now the melting-point of an unknown substance, we obtain the extension corresponding to its point of melting and scale from the chart the temperature proper to this extension. This is all that is required to determine the melting-points of minerals to the degree of accuracy attained in the elaborate researches of Carnelley and Violle. Although the extensions, as determined directly, may be thus used to determine unknown temperatures, it is preferable to plot in each case the ratio of the extension to the original length of the ribbon, or the quantity $l_2 - l_1/l_1$, this value being independent of the length of ribbon used in making the experiments, a length which it is inconvenient to regulate to uniformity on all occasions. The value of this fraction is certainly applicable to all observations made with platinum of the one quality, or to the contents of the one reel if certain precautions be taken which will be described later. In this way a curve once plotted may be kept in use for many observations. The chart accompanying this paper is plotted in this manner.

(To be continued.)

AN ALLOY OF TIN AND SODIUM WITH A DEFINITE COMPOSITION.

By HENRY BAILEY.

In a recent endeavour to prepare an allotropic modification of tin by acting on its sodium alloy with water, I was struck by the uniformity in appearance and behaviour of several of my alloys to which an excess of sodium had been added, and which had been subjected for a considerable time to a high temperature. A quantity of this substance was prepared by mixing together tin and sodium (the sodium being in excess) in a crucible provided with a luted lid, through which a small hole had been drilled so as to allow the excess of sodium to escape as vapour. Air was excluded by means of a lump of charcoal being placed loosely over the hole. The crucible and its contents were then heated for a considerable time until it was judged that all sodium existing as such was volatilised. After cooling in an inert atmosphere, the content of the crucible was extracted, and was found to consist of a very brittle mass externally covered with a slight white scoria, which on fracture revealed brilliant crystalline,—in fact almost crystallised facets, of a beautiful bronze colour, quickly becoming tarnished with a grey powder. An analysis of the compound gave percentages which corresponded exactly with the formula Na_2Sn, showing it to be of the type of stannous compounds represented by the oxide SnO. The action of this substance on water is interesting from a teacher's point of view; it being specifically heavier than water, quantities of hydrogen can be safely prepared for class demonstrations. An excess of sodium gave an alloy which decomposed water with such violence that the hydrogen evolved was ignited, the heat of combination being localised owing to the specific gravity of the alloy. To ensure that the temperature used in the preparation of the alloy was sufficient to volatilise the free sodium, a quantity of pure sodium was heated in a crucible with the necessary precautions for the exclusion of air, at the same temperature as that used in the preparation of the compound. As a result only a slight trace of oxide was obtained.

Science School, Penzance,
December 23, 1891.

A READY METHOD OF DISTINGUISHING BETWEEN ALPHA- AND BETA-NAPHTHOL.

By F. W. RICHARDSON, F.C.S., &c.

Having occasion to test the contents of two bottles to ascertain which was alpha- and which beta-naphthol, I applied the methods of N. Yvon, described in the CHEMICAL NEWS (vol. lxiv., p. 321), but obtained very unsatisfactory results; indeed process (2), as might be expected, gave no result whatever.

Remembering that the difference between the azo-dyes "Orange I." and "Orange II." is entirely due to the fact that while for the preparation of the former dye α-naphthol is used, β-naphthol is required for the latter, I worked out the following process:—

Dissolve about 5 c.grms. of sulphanilic acid in a little water containing about 5 c.c. of normal soda; add 5 c.c.

of normal sulphuric acid, and mix the solution with 2 c.grms. of sodium nitrite dissolved in a few drops of water.

Dissolve a little (about 4 c.grms.) of the naphthol by the aid of a few drops (0·5 c.c.) of normal soda, and into this solution pour the diazotised sulphanilic acid. With α-naphthol the liquid becomes dark blood-red; with β naphthol only a reddish-yellow colour is produced; this difference is most marked when the dyes are salted out.

The α-naphthol dye becomes dark brown with dilute sulphuric acid, while the β-naphthol compound is quite unchanged: this last reaction is very distinctive.

The equations representing the changes which take place are as follows:—

$$\underset{\text{Sulphanilic acid.}}{C_6H_4.HSO_3.NH_2} + 2HCl + NaNO_2 = NaCl + 2H_2O +$$

$$+ \underset{\text{Diazobenzol-sulphonic acid chloride.}}{C_6H_4.HSO_3.N=N-Cl}.$$

$$C_6H_4.HSO_3.N=N-Cl + 2NaHO + \underset{\text{Naphthol.}}{C_{10}H_7(HO)} = NaCl +$$

$$+ 2H_2O + C_6H_4 \begin{cases} N=N-\underset{\text{Orange I. or Orange II.}}{C_{10}H_6(OH)\ (\alpha \text{ or } \beta)} \\ NaSO_3. \end{cases}$$

Sodiumnaphtholdiazobenzene-sulphonate.

A TABULAR EXPRESSION OF THE PERIODIC RELATIONS OF THE ELEMENTS.

By HENRY BASSETT.

(Concluded from p. 4).

THE third fold of the paper covers up Ta and W, and we get the following:—

TABLE III.

Li	Na	K	Rb	?	?
Be	Mg	Ca	Sr	?	?
B	Al	Sc	Y	Tb	?
C	Si	Ti	Zr	Ho	?
N	P	V	Nb	?	?
O	S	Cr	Mo	Er	?
F	Cl	Mn	?	?	?

Our knowledge of the general chemical characters of the rare earth-metals, now found to the right of the table, is far too slight at present to warrant many remarks, but Tb, which gives a strongly basic oxide, appropriately follows Y, and Er, Mo, and Cr have at least one well-marked similarity, that of forming strongly-coloured compounds, and I cannot but think it probable that further investigation may show other analogies in this part of the primary table also.

The last fold of the paper covers up Tb, Ho, and Er, and we finally obtain:—

TABLE IV.

Li	Na	K	Rb	Cs	?
Be	Mg	Ca	Sr	Ba	?
B	Al	Sc	Y	La	?
C	Si	Ti	Zr	Ce	Th
N	P	V	Nb	Ndy	?
O	S	Cr	Mo	Pdy	U
F	Cl	Mn	?	?	?

Now at last we see all the alkali metals in an unbroken series; then we have Be, Mg, and the alkaline earth metals all together, followed by a complete series of 3-valent elements showing very close analogies, and a regular gradation of properties from left to right. In the lower part of the table the resemblances are less pronounced, but we cannot overlook the conjunction of a still larger number of colorific elements than in Table III. The Tables I. and IV. are, in fact, complementary, the closest analogies and most complete gradation being shown in the three bottom lines in the former, and in the three top lines in the latter.

It will be readily seen that this series of tables is actually derived from the first by successive upward shifts of the first and second pairs of groups or periods, and I have devised a sliding model for the illustration of the complete system, which appears to agree with facts as far as we know them, and to give a simple, clear, and suggestive expression of the relations of the first typical small periods with the succeeding large ones, and with the other small periods of which these are built up. Many points of interest will present themselves on examination of the primary table, but their discussion would unduly extend this paper, and would besides be premature.

By calling H the first period, the old distinguishing numbers of the others, so well known to students of Mendeleeff's table, would be retained; but surely the term must imply a group of elements? If any such existed between H and Li the resulting period would show very little numerical analogy with any of the others, and, from this and some other considerations, I am inclined to think that hydrogen might, without great impropriety, be called the Anteperiodic element. I will not pursue the subject, but it is one on which the ghost of Prout would certainly have a great deal to say.

One important point remains. While the atomic weights are the prime foundation of the system, the atomic volumes are also of great value from the direct indications which they give as to the simple or complex character of the periods. Starting from the highest member of a period, whether single or double, they gradually diminish to some intermediate or central point, and then increase to the lowest. The quadruple Cs period given in the primary table above should function as a whole from this point of view, like the two preceding double periods. I consider there are some indications that it will be found to do so, and to have its minimum in the Os interperiodic group, but for proof of this many essential data are at present wanting. There is very little doubt that metallic Ta has not been prepared, and the upper members are also unknown in the metallic state till we reach Di. We must therefore await determinations of the specific gravities of Ta, and of some few of the higher members, say Yb, Er, and Sm. The atomic volumes of Th and U, the only known members of the following series, seem to show that they belong to a double period, which I have indicated in the table.

At a meeting of the Franklin Institute, on Sept. 15th, 1891, Mr. Waldron Shapleigh exhibited a magnificent collection of salts of the rare earths, and called attention to the fact that many of them would be rare no longer, hundreds of tons of their ores existing in North Carolina, Brazil, and elsewhere (CHEM. NEWS, Nov. 6, 1891). We may, therefore, confidently anticipate that the missing data will be forthcoming in the near future from the researches of the many distinguished workers who have already done so much towards the elucidation of a subject which is perhaps one of the most interesting and important occupying the attention of the chemical world.

FUNDAMENTAL PRINCIPLES TO SERVE IN THE CHEMICAL EXAMINATION OF WINES, AND IN THE JUDGMENT TO BE PASSED UPON THEM.

By W. FRESENIUS and B. HAAS.

A. *Chemical Examination.*

1. FOR the determination of the specific gravity a pycnometric examination at 15° C. is to serve as the basis; it must be given accurately to four decimal places.

2. The results must be given in grammes per 100 c.c., or per litre.

3. The alcohol is to be determined by the distillation method; the specific gravity of the weighed distillate is

taken with the pycnometer at 15° C. (respectively 15·5° and the proportion of alcohol calculated accordingly).

4. The proportion of extract:—(*a*). Of wines with an extract amounting to 3 grms. per 100 c.c., 50 c.c. are evaporated in a flat-bottomed platinum capsule upon the water-bath; the residue is heated for 2½ hours in water drying niche, and finally cooled in the exsiccator and weighed. (*b*). Wines containing a higher proportion of extract are to be diluted with water, so as not to contain more than 3 grms. extract in 100 c.c. The residue is to be treated as above. (*c*). For sweet wines an indirect method of determining the extract from the sp. gr. of the wine after removal of the alcohol is to be preferred.

5. The free acid is determined by titration with potassa- or soda-lye suitably diluted, using litmus-paper as indicator, and calculating the result as tartaric acid ($C_4H_6O_6$). Volatile acids are to be determined by distillation in watery vapour, and to be expressed as acetic acid ($C_2H_4O_2$).

6. The determination of the glycerin in ordinary wines (not sweet wines) is to be carried out according to the method agreed on by the German or Austrian chemists, without a correction for evaporation. The determination of glycerin in sweet wines does not give accurate results. If required, Borgmann's method is to be preferred.

7. Mineral matter is found by incinerating the residue from the evaporation of 50 c.c.

8. Polarisation may often be dispensed with in dry wines; in sweet wines it must be resorted to before and after inversion.

9. Sugar is to be determined according to Soxhlet or Allihn, and expressed as grape-sugar. If the proportion of sugar is considerable, or if the difference between the proportion of extract and the quantity of directly reductive sugar is exceptionally high, a determination of sugar must be carried out after inversion.

10. Sulphuric acid is precipitated directly with barium chloride in wine acidulated with hydrochloric acid, and determined in the ordinary manner.

11. Sulphurous acid is determined by distilling a portion of the wine to which phosphoric acid has been added, receiving the distillate in solution of iodine, and determining the sulphuric acid thus formed.

12. The determination of phosphoric acid is to be effected in the ash of the molybdic method.

13. Tartar is to be determined by Nessler and Barth's method.

14. A determination of free tartaric acid takes place only if required to complete the other analytical results. A mere qualitative detection is useless. For the qualitative determination of free tartaric acid along with that of tartar the method of B. Haas (*Zeit. Nahrungsmittel und Hygiene*, 1888, p. 100) is recommended.

15. Examination for Colouring-matters:—(*a*). Vegetable colours. The wine is mixed with an excess of lead acetate and filtered. The colour of the precipitate in a genuine red wine may be greyish-blue, bluish-grey, ash-colour, or greenish. If a precipitate is obtained not greatly differing from these colours, the search for other vegetable pigments can give no certain result. The colouring-matter of bilberries give a blue precipitate; mallow and elder berries a green. The colour of phytolacca berries differs from that of red wine by giving a red-violet precipitate with lead. (*b*). Tar colours. As the colouring of any article of food, &c., with tar colours is illegal, it is sufficient to prove the presence of any such colouring matter in wine. In most cases a tar colour may be recognised in wine by the following three methods:—

α. By shaking the filtrate from the basic lead acetate with amylic alcohol, and testing the coloured amylic alcohol. For this purpose we require 100 c.c. of wine and 30 c.c. of solution of basic lead acetate.

β. By the wool test according to Strohmer and Arata (dyeing wool).

γ. By Cazeneuve's mercuric-oxide test (*Vierteljahrschrift fur Chemie der Nahrungsmittel*, 1886, p. 80.

The following two tests are recommended in addition:—

δ. Shaking the wine with ether before and after supersaturation with ammonia.

ε. A similar shaking with amylic alcohol.

16. Salicylic acid is best sought for by shaking the wine up with carbon disulphide in a mixture of equal volumes of ether and petroleum ether, evaporating down and testing the residue with ferric chloride. If much more than 100 c.c. of wine are used, a faint colour may be occasioned by the normal constituents of wine.

17. For detecting saccharine C. Schmitt's method is recommended. The wine is shaken up with a mixture of equal parts of ether and petroleum ether, and the evaporated residue is melted with sodium hydroxide. Not more than 100 c.c. of wine must be used for this test.

18. Nitric acid is sought for by adding 1 to 3 drops of wine to a solution of diphenylamine in (pure) concentrated sulphuric acid.—*Zeitschrift fur Anal. Chemie*, xxx., Part 4.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 5).

Hence it follows, as a matter of course, that so-called contact effects, like, *e.g.*, the reaction between wood-charcoal which has absorbed chlorine and hydrogen conveyed in darkness is introduced by the high tensions and consequent condensations in the spaces of the charcoal which are in part capillary and in part very uneven, possessing a very large surface, in which spaces the reaction takes place.

The much disputed action of platinum black is without any doubt analogous. Gases—especially atmospheric air, watery vapour, &c.—are condensed upon the extremely porous or finely divided platinum, and the atmospheric oxygen becomes thus extremely capable of reaction, and is transformed into an active so-called allotropic state.

It is common to all these reactions and conversions that capillary spaces occur in very porous third bodies in which the substances capable of reaction undergo great condensation.

In all such cases there is given the possibility, even the probability,—we might in some instances say the necessity,—of an intense chemical action which must be proportional to the magnitude of the tension.

In capillary spaces there can take place from a certain size onward merely an ordinary chemical process, since below a certain size, capable of being experimentally determined, no action of mass is possible. Action of mass is possible only where masses are possible, therefore with a certain number of mols. Such truly capillary spaces where the mols. cannot accumulate up to the number necessary for effecting an ordinary chemical reaction exclude an action of masses, a chemical equilibrium, and they are the field for true condensations, for the most intense chemical transformations, for spontaneous decomposition. Here there occur, in place of the coarse reaction of masses, the most subtile individual reactions, as we may call them. Here there do not meet large armies of mols. with the corresponding partial pressures; there occurs here, the rather, an active and continual single combat, a splitting up of the mols. as they come in the scope of the atoms engaged in violent competition for their affinities. No equalisation of the entire atomic energy present, no maximum of entropy, is possible. On the contrary, other internal relations, *e.g.*, between the height reached, consequently the ascending force and the molecular weights come into their rights. A number of true chemical compounds fall as dead material out of the

incessant chemism going on connected with the first five accompanying phenomena already enumerated, whilst of the accessory material only a strictly defined portion conditioned by affinity arrives at scission and synthesis.

But this individual chemical reaction is totally distinct from the chemical mass reaction in the test-tube, in the retort, in the flask. An entire series of physical conditions are here of the greatest influence, which are there unimportant, *e.g.*, the presence or absence of light, the fluctuation of temperature for the fraction of a degree, the greater or less elasticity of the sides of the containing vessels, agitation, and other conditions which are compensated in mass reaction, but not in individual reaction.

The entire consideration thus laid down can be completely applied to the chemism of living protoplasm. Here there certainly occurs not exclusively a chemical mass reaction, but principally a chemical reaction individualised in the highest degree, since the microscopic minuteness of the spaces does not permit of mass reaction.

The system of unenclosed capillaries of the network in protoplasm (the latter matter having been first made known by Karl Frommann in a series of admirable investigations), the intervals and the minutest vacuola, with their fissures often remarkably permanent and often as remarkably mutable, are to be regarded as the true seat of chemical transformation in protoplasm, and hence in the organism altogether. Even when non-capillary tubes are recognised in such protoplasm as bands with a double outline—the universal occurrence of such must be excluded—it is inconceivable that sideless channels and fissures, exceeding in fineness all ordinary capillaries, should not be present in every protoplasm in which a reticulated structure can be detected. That no protoplasm can exist without such a structure is almost universally admitted. That in presence of the nuclear division figures recognised by numerous observers with the most satisfactory agreement, in view of the mutations of the finer structure of protoplasms observed in embryonal as in developed, in animal as in vegetal, in normal as in pathological, tissues, the existence of the finest capillaries of vacuola or capillary fissures in the highest degree cannot be contested. For the different nature of the solid and liquid parts of the nucleus, of the nuclear membrane, the hyaline border, and even the cell-membrane itself, exclude the possibility of homogeneity existing, notwithstanding the constant presence of a reticular structure within any given protoplasmic tissue.

(To be continued.)

NITROHYDRIC ACID.

By TH. CURTIUS.

(Concluded from p. 5.)

NITROGEN AMMONIUM is precipitated from its alcoholic solution by ether as a snow-white powder, consisting of minute, anisotropic needles. If this powder is boiled for some time in absolute alcohol in a reflux-condenser it is entirely dissolved. On cooling, the substance separates out in large, massive, colourless leaflets, composed of individual crystals arranged in the form of stairs or of a fan. In this state the substance has a deceptive resemblance to ammonium chloride. It does not, however, crystallise in the regular system. From water, on evaporation *in vacuo*, we may obtain it in the form of large crystals, limpid as water, which become dull on exposure to the air. Nitrogen ammonium reacts faintly alkaline; it is not hygroscopic, dissolves readily in water and in alcohol at 80 per cent. It is sparingly soluble in absolute alcohol and insoluble in ether or benzene. It is distinguished by its extreme volatility, whether along with the vapours of alcohol or water or if preserved alone. If exposed to the air it disappears entirely by degrees, bu without any change. If gently heated a little above 100°, it may be sublimed from one place to another exactly like ammonium chloride, and is thus obtained in small glittering prisms. If rapidly heated in an open test-tube, it explodes with extreme violence.

Nitrogen Diammonium, N_5H_5 (*Diammoniummonoazide*).

Diamide ought to unite with one or with two mols. of nitrohydric acid to form the salts N_5H_5 and N_8H_6. Hitherto I have only succeeded in obtaining N_5H_5. It is prepared by superstratifying nitrogen ammonium with one mol. of hydrazine hydrate, and evaporating in the exsiccator in a shallow capsule. Further, very concentrated aqueous nitrohydric acid (obtained by distilling 60 grms. nitrogen lead with dilute sulphuric acid and watery vapour) mixed with hydrazine hydrate until litmus was turned distinctly blue, when the solution was left to spontaneous evaporation over potassa or sulphuric acid. Here also N_5H_5 crystallised out in place of N_8H_6 as it was expected, whilst nitrohydrogen was in part volatilised and absorbed by the caustic potassa under the bell. For analysis the substance was re-crystallised from alcohol.

On combustion in a current of oxygen, the salt exploded every time with extreme violence. But the nitrogen also could not be determined volumetrically by combustion along with copper oxide in a current of carbon dioxide, as on displacement of the air a large part of the substance was always volatilised. The compound was therefore dissolved in water, and its proportion of nitrohydric acid was precipitated as nitrogen silver by silver nitrate after the addition of a few drops of nitric acid. The substance, which is extremely hygroscopic, is effected in closed tubes. The precipitated nitrogen metal was first dried by section upon a weighed, perforated, porcelain capsule, and its desiccation was cautiously completed at 100°.

0·4949 grm. of the substance, dried over potassa lye and sulphuric acid, yielded, on precipitation with silver nitrate, 0·9727 AgN_3, corresponding to 0·2818 grm. nitrohydrogen.

	Calculated for $N_5H.N_5H_4$.	Found.
N_3H 43	57·35	56·95

An attempt was made to shake out the base combined with the acid in the nitric filtrate from nitrogen silver by the cautious addition of benzaldehyde. As soon as an excess of this solvent was added a portion of the benzalazine formed re-dissolved in the liquid containing benzaldehyde, so that the quantity of diamide found was smaller than that which the ascertained acidity of the salt required.

Nitrogen diammonium (diammoniummonoazide), N_5H_5, crystallises in stout anisotropic prisms, an inch in length and of a vitreous lustre; they melt at about 50°, deliquesce in a short time in the air, and gradually evaporate at common temperatures, but more rapidly along with the vapours of alcohol or water. They are sparingly soluble in boiling alcohol, from which they crystallise in shining leaves. The crystals burn quietly with a smoky flame, of a slightly yellow colour if kindled with a flame without leaving traces of soot or residue. Metallic surfaces upon which this combustion takes place are freed from every trace of oxide by the reductive action of the ignited hydrogen evolved, and appear as if polished.

On rapid heating in the air, as on contact with a wire heated to whiteness, or on ignition by means of detonating nitrogen metals or fulminates, there occurs a fearful explosion. Even in the moist deliquesced condition, these explosive properties are retained.—*Berichte der Deutschen Chemischen Gesellschaft*, vol. xxiv., pp. 33-41.

Determination of Lignine in Woods.—R. Benedikt and M. Bamberger.—(*Monatshefte für Chemie.*)—As Benedikt and Grüssner employ the so-called methyl number for the recognition of oils, fats, and waxes, the authors aim at discovering the percentage of lignine in a wood by means of its methyl number. They give a tabular conspectus of their results.

THE DETECTION AND DETERMINATION OF POTASSIUM SPECTROSCOPICALLY.*

By F. A. GOOCH and T. S. HART.

Bunsen and Kirchhoff originally determined the delicacy of the spectroscopic test for potassium by exploding in a darkened room a mixture of potassium chlorate with milk sugar, and observing the amount of finely divided chloride which it was necessary to diffuse through the given space in order to bring out unmistakably the spectrum of the metal. These investigators were able to state that the presence of no more than 1-1000 of a m.grm. of the potassium salt is sufficient to give to the flame the characteristic spectrum of the element. By similar methods the delicacy of the tests for lithium carbonate and sodium chlorate were shown to be a thousand times and three thousand times as delicate respectively. Practically, the detection of lithium and sodium spectroscopically is extremely easy and satisfactory, the only difficulty being that the exceeding delicacy of the sodium test, and the ubiquitousness of sodium salts often make a decision doubtful as to whether that element is present essentially in the substance under examination or by accident. With potassium the case is different, and experience shows that when the test is to be made for very small amounts of potassium, the simple method in vogue for developing the luminosity of lithium and sodium—the dipping of a single loop of platinum wire in the liquid or solid substance, and the placing of the loop in the Bunsen flame—fails, because, as it seems to us, so great a proportion of the material is dispersed before the heat of the flame effects the dissociation of the metal which precedes the production of the spectrum.

We have endeavoured to improve the conditions of exposure of the test substance by making use of more powerful flames and by substituting for the single loop the hollow coils of platinum wire first recommended, so far as has come to our knowledge, by Truchot (*Comp. Rend.*, lxxviii., 1022) in the description of a method for the quantitative determination of lithium. Such coils are easily made by winding the wire somewhat obliquely about a rod of suitable size, pressing the coils close together, and gathering the free ends into a twisted handle. The size of the coils is adjustable without difficulty, so that each coil may be made to hold almost exactly any appropriate amount, and to take up this amount with very little variation in successive fillings, provided only that the precaution be taken in the process of filling to plunge the coil while hot into the liquid, and to keep its axis inclined obliquely to the surface of the liquid while withdrawing it. How closely the capacity of such coils may be adjusted, and how uniformly they may be filled, is shown in the figures of the accompanying record.

Weight of—	I. Grm.	II. Grm.	III. Grm.	IV. Grm.	V. Grm.	VI. Grm.
Filled coil—						
	0·1996	0·2780	0·2794	0·2844	0·3572	0·3296
	0·1996	0·2780	0·2794	0·2845	0·3571	0·3296
	0·1996	0·2780	0·2794	0·2844	0·3572	0·3298
	0·1996	0·2780	0·2794	0·2845	0·3571	0·3298
	0·1996	0·2781	0·2794	0·2844	0·2571	0·3296
Empty coil—						
	0·1986	0·2760	0·2764	0·2804	0·3521	0·3100
Contents (mean)—						
	0·0010	0·00202	0·0030	0·00404	0·00504	0·01968

It is plain that we have in these coils simple means of taking up known amounts of material in solution; and by gentle heating, the liquid may be evaporated and the solid material left thinly and uniformly spread, not easily detachable, and so in condition to be acted upon with effect when brought to the flame. The evaporation may be conducted with little danger of loss of material by holding the handle of the coil across the flame with the coil proper at a safe distance outside; but we have generally, and preferably, used a hot radiator, over which the coils are exposed, the handles resting upon a flat asbestos ring. The burner which we have used in heating the coils before the spectroscope is of the Muencke pattern, and gives a powerful flame 3 c.m. wide at its base. We have generally adjusted the flame to a height of 20 c.m., and have introduced the coil, after thorough drying, just within the outer mantle, on the side next the spectroscope, with the axis transverse to the slit of the spectroscope and the handle across the body of the flame. In cleaning the coils we have found it convenient to heat them in the flame of an Argand burner of the Fletcher pattern, beneath which is burned in a small lamp alcohol containing about a twentieth of its volume of chloroform. The products of combustion of the alcohol and chloroform are conveyed to the interior of the flame above by a glass funnel fitted by a cork to the tube of the Argand burner. This arrangement of apparatus gives a hot colourless flame through which hydrochloric acid is constantly diffused in condition to clean the wires completely and without attention. The spectroscope which we have employed is a well made single prism instrument provided with a scale and a movable observing telescope, so that different portions of the spectrum may be viewed or cut off at will. The slit is adjustable, but for measuring its width we have been obliged to have recourse to the device of closing it upon wires of known gauge. Our work has been done in the ordinary diffused light of the laboratory, care having been taken to cut off from the room direct sunlight only; but in observing it has been our custom to shield the eye in use as completely as possible with the hand or with a dark handkerchief, and to cover the eye not in use. We have found it desirable to use the scale of the instrument, illuminated to the lowest degree of visibility, to aid the eye in placing barely visible lines.

Upon experimenting with the apparatus described, it was found that the largest coil used was best adapted to our purpose, and, accordingly, in all the experiments made subsequently and recorded in the following account, coils holding 1-50 of a grm. of water, measuring 2 m.m. in diameter by 1 c.m. in length, made of No. 28 wire (0·32 m.m. in diameter), and wound in about thirty turns, were the ones employed. With these coils and the flame adjusted to a height of 20 c.m. we have been able to recognise the presence of potassium, taken in the form of the chloride, in a coil-full of liquid containing 0·00066 grm. of the metal in 10 c.m.^{3}, when the slit had a width of 0·18 m.m., and containing 0·0005 grm. in the same volume of solution, when the slit was set 0·23 m.m. wide. That is to say, 1-750 m.grm. of potassium to the coil-full produces a line distinctly visible with a slit of 0·18 m.m., and 1-1000 m.grm. with a slit of 0·23 m.m., and it is evident that this practical method of producing the spectrum of potassium gives results of a delicacy approaching that indicated in the experiments of Bunsen and Kirchhoff.

These determinations were made with pure potassium chloride carefully prepared from the chlorate, but in practical analysis it almost always happens that sodium is also present. Experiments were therefore made to determine the influence of varying amounts of the latter upon the visibility of the potassium line. The dilution of the potassium chloride was adjusted nearly to the last limit of visibility, so that a coil-full of the liquid should contain 1-700 m.grm., or 1-1000 m.grm. of the element, according as the slit was 0·18 m.m. or 0·23 m.m. wide; to this solution were added weighed amounts of pure sodium chloride twice re-precipitated and washed by hydrochloric acid, and the spectroscopic tests were carried out as before, the sodium line being kept within the field of view with the potassium line.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlii., December, 1891.

Weight of K in a coil-full. M.grm.	Weight of Na in a coil-full. M.grm.	Ratio of Na : K.	Width of slit. M.m.	Number of trials.	Characteristic of line.
0·0010	0·0000	0 : 1	0·23	3	visible
0·0010	0·0020	2 : 1	0·23	3	,,
0·0010	0·0100	10 : 1	0·23	3	,,
0·0010	0·0200	20 : 1	0·23	3	,,
0·0010	0·0400	40 : 1	0·23	3	,,
0·0010	0·0500	50 : 1	0·23	4	very faint or none
0·0010	0·1000	100 : 1	0·23	3	none
0·0010	0·2000	200 : 1	0·23	3	,,
0·0014	0·0000	0 : 1	0·18	3	visible
0·0014	0·0560	40 : 1	0·18	3	,,
0·0014	0·0700	50 : 1	0·18	3	,,
0·0014	0·1400	100 : 1	0·18	2	,,
0·0014	0·1400	100 : 1	0·18	2	none

It is obvious from these results that a considerable amount of sodium may be present in the flame when the sodium line is in full view in the spectrum, and the slit adjusted to nearly the lowest limit of visibility of pure potassium, without interfering with the appearance of the potassium line, but that a quantity of sodium amounting to a hundred times that of the potassium is sufficient to entirely overpower the spectrum of the potassium. The inference is plain that the proportion of sodium to potassium should not be permitted to reach 100 : 1 when it is desirable to bring out the full delicacy of the spectroscopic test with the sodium line in the field of view. When too great a proportion of sodium is present, its influence may be moderated by throwing the sodium line out of view, if the instrument in use possesses the necessary adjustment; otherwise, it is easy to effect a partial separation of the sodium chloride from the potassium chloride, before bringing the solution to the test, by precipitating with alcohol. Our experience shows that the delicacy of the test for potassium is not impaired materially by such treatment of the mixed chlorides. We found, for example, that 0·0070 grm. of potassium chloride mixed with 0·5 grm. of pure sodium chloride, dissolved in the least amount of water, and extracted carefully by about 7 c.m.^{3} of absolute alcohol applied in successive portions, was so completely retained in solution and separated from sodium, that a coil-full taken from the solution diluted to 140 c.m.^{3} gave the spectroscopic test for potassium distinctly with the slit at 0·23 m.m. In this case, at least, the treatment did not diminish the delicacy of the test; for, a coil-full of the diluted solution could not have contained more than 1-1000th m.grm of potassium, if nothing had been lost. It was found, in like manner, that, by taking pains to evaporate the alcoholic extract, and to dissolve the residue in a drop of water, 0·0001 grm. of potassium originally present as the chloride with 0·5 grm. of sodium chloride, was easily found. By turning the observing telescope so as to cut off as completely as possible the sodium light, we were able to detect potassium in four successive tests of a drop of the final solution which was just large enough to fill the coil four times, when the original amount of potassium present with 0·5 grm. of sodium chloride was 0·00001 grm. This is equivalent to detecting 1-400th m.grm. of potassium in a drop large enough to fill the coil once. We were assured of the entire absence of potassium from the sodium chloride which we used by the fact that the similar extraction of 1 grm. of the salt by alcohol left a residue which yielded no line of potassium when examined spectroscopically. It is, perhaps, worth noting, in passing, that the coil may be made to pick up a drop of a size only sufficient to fill it by simply touching the coil while hissing hot to the drop.

Certain experiments in which the method of manipulation which we have described was applied to the determination of potassium salts other than the chloride indicated that the test is less delicate in the case of the sulphate, and rather more delicate in the case of the carbonate. We were able to find the red line of potassium unmistakably, when only 1-2000th of a milligrm. of potassium was introduced into the flame in the form of the carbonate.

The quantitative determination of potassium by the spectroscope has never, so far as we know, been accomplished heretofore. Sodium appears to have been successfully estimated by Champion, Pellet, and Grenier (*Compt. Rend.*, lxxvi., 707) by the use of comparison flames, produced by the aid of complex mechanism, and a spectrophotometer of original construction. Lithium has been determined more simply, Truchot (*Compt. Rend.*, lxxviii., 1022) having been the first to suggest a method of manipulation which was modified by Ballmann (*Zeitschr. für Anal. Chem.*, xiv., 297) and taken up later by Bell (*Am. Chem. Jour.*, vii., 35) apparently without knowledge of the previous work on the same line. Truchot's method consists in comparing the duration and strength of the spectral lines developed by exposure to the Bunsen flame of portions taken up in a platinum loop from the test-solution and standard solutions of different strength. No analytical proofs of the value of the method were given, and accuracy was not claimed beyond the recognition of differences of from three to four milligrms. in a litre of liquid when amounts not exceeding forty milligrms. per litre were compared. Ballmann discards as valueless the observation of the duration of the spectral line, advocates the dilution of the test and standard solutions to the absolute extinction of the line, and employs hollow cones, measuring 2·5 m.m. by 3·5 m.m., to carry the liquids to the flame. Bell follows Ballmann's method of diluting the solutions to be compared to a common condition, but takes the vanishing point of the line instead of the point of absolute invisibility, and makes his loops of platinum very small. Both Ballmann and Bell were able to estimate thallium similarly, but neither determined potassium, Bell declaring specifically that the method is inapplicable to the handling of that element.

Our success in determining potassium qualitatively by the use of powerful flames and coils of large dimensions was such as to encourage the attempt to apply quantitatively the same method of manipulating; and from certain preliminary experiments looking in this direction we found it best, for our purpose at least, to fall back upon Truchot's method of comparing visible lines, rather than to try to fix the vanishing point or the point of extinction of the spectral line. We chose a dilution of the standard solution which corresponds to the presence of 1-500th m.g. of potassium to the coil-full, and set the slit at a width of 0·23 m.m., having found it most advantageous to work with lines for comparison bright enough to be visible without much effort. Our mode of proceeding is to dilute the test-solution until the line given by the potassium contained in a coil-full is of the same brightness as that given by the same quantity of the standard solution. From the final volume of the test solution the quantity of potassium present in it is directly calculable; for, since any given volume of the test-solution at its final dilution contains exactly the same amount of potassium as the same volume of the standard solution, we have only to multiply the number expressing the volume in cubic centimetres of the test-solution by the weight in grammes of the potassium contained in one cubic centimetre of the standard in order to obtain the weight in grammes of potassium in the whole test-solution. We found it convenient to use several coils adjusted to the same capacity, and to clean, fill, dry, and ignite them before the spectroscope in the manner previously described. From time to time the capacity of the coils should be readjusted, or else the final comparison tests should be made with a single coil. It is essential that the eye of the observer should be kept as nearly as possible in the same condition of sensitiveness and in the same position in making the comparisons, and to accomplish this end we found it best to hold the eye at the observing telescope during the entire interval between the exposures, to shade it care-

fully by the hand, or otherwise, to cover the eye not in use, to cut off all direct sun-light from the work-table (though the diffused light of the room is not objectionable), and to light the comparison scale of the spectroscope to the faintest possible visibility in order to fix exactly the position in which the line is to be sought. It is important, too, that the trials of the test and standard should come as closely together as possible in point of time. The observations of a series should be made by the same individual, the preparation and exposure of the wires being made by another. It is not possible to attain the best results in such work single-handed. The dilution of the test-solution is made conveniently, and with sufficient accuracy, in 100 c.m.³ cylinders graduated to half cubic centimetres, the mixture being made thorough by passing the solution from vessel to vessel. It is often advantageous to divide a liquid which is to be diluted, and to work with aliquot portions, so that it may be possible to retrace a step without trouble in case a portion of the solution has been unwittingly diluted too much; such a mode of proceeding is, of course, necessary when the final dilution must exceed 100 c.m.³, unless large graduates are called into use. Excepting the cases of very concentrated solutions, no significant loss of material is occasioned by the filling of the coils, the error thus introduced being trivial in comparison with that inherent in all photometric processes. The following is the record of our experience in the comparison of solutions of pure potassium chloride, the strength of the test solution being unknown to the observer.

Experiment I.

Volume of test-solution.	Characteristic of line compared with standard.
20 c.m.³	stronger
50 ,,	stronger
100 ,,	stronger
110 ,,	stronger
120 ,,	stronger
150 ,,	like
200 ,,	weaker
160 ,,	weaker
150 ,,	like

Experiment II.

Volume of test-solution.	Characteristic of line compared with standard.
30 c.m.³	stronger
60 ,,	stronger
82 ,,	weaker
70 ,,	stronger
76 ,,	stronger
78 ,,	stronger
80 ,,	like

(150 × 0·0001 = 0·0150)		(80 × 0·0001 = 0·0080)	
Potassium found	0·0150 grm.	Potassium found	0·0080
,, taken	0·0150 ,,	,, taken	0·0080
Limits on either side	0·0120 ,, 0·0160 ,,	Limits on either side	0·0078 ,, 0·0082 ,,
Error..	0·0000 ,,	Error	0·0000

These results show a degree of accuracy in the process quite unexpected. In the former no attempt was made to approximate as closely as possible to the limits of dilution on both sides of the condition of equal brightness in test and standard, but in the latter great care was taken in this respect, and the possible error cannot exceed two and a half per cent of the entire amount of potassium involved.

(To be continued).

CORRESPONDENCE.

DANGERS OF WEED-KILLERS."

To the Editor of the Chemical News.

Sir,—My attention has been called to a paragraph in the Chemical News (vol. lxiv., p. 265) commenting on the dangerous practice of selling to ignorant workmen casks of arsenical preparations as "weed-killers."

I can fully confirm the statement made as to the prevalence of this procedure. Some time since I was consulted by a client, who made such weed-killers, as to the easiest mode of obtaining an arsenical preparation in a convenient form. Of course I gave him the chemical advice required, but at the same time I felt bound to remonstrate with him on the danger accruing from such practice; and I am happy to say that, consequent on my protest, he abandoned the use of arsenic.

As a matter of fact I suggested that he should first of all take legal advice as to his qualification for selling arsenic as simply "weed-killer," and, as I had fully anticipated, the reply was adverse to him. Under these circumstances it would seem very desirable that any manufacturers who may be still selling arsenic, without any adequate caution, as "weed-killer," should be brought to book. I will only add that the arsenic is in the very soluble—and therefore especially dangerous—form of arsenite of soda.—I am, &c.,

F. H. Perry Coste.

Analytical Laboratory, 7, Fowkes Buildings, Great Tower St., E.C., Dec. 29, 1891.

THE NEW METHYLATED SPIRIT.

To the Editor of the Chemical News.

Sir,—May I offer a suggestion with regard to this matter? We may assume that the Revenue authorities have no object in view save the prevention of drinking alcohol which has been allowed to pass duty free, for it can hardly be possible that they are taking this action, so plainly against the interest of very many people, merely with a view of increasing the Revenue.

Ought they not, therefore, to be ready to allow the spirit to be sold to all persons who are ready to enter their names (accompanied if necessary by references) in a book kept by the tradesman supplying the spirit, which book could be inspected by the Revenue officer?

Or, if this course is not sufficiently stringent, might not a license at a small sum (say 3s. or 4s. per annum) be issued to persons applying for the authority to purchase and use the spirit for stated purposes?

Unless some such modification is allowed by the Revenue their action must tend tend to check research of many kinds, and injure the position of industrial chemists.—I am, &c.,

C. G. Moor.

Vicarage, St. Clement, near Truro, Jan. 2, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiii., No. 25, December 21, 1891.

This issue gives an account of the annual public session of the Academy held on December 21, 1891, for the purpose of awarding the numerous prizes at its disposal for scientific researches.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 8, October 20, 1891.

This issue contains merely abstracts from other journals.

Series 3, Vol. vi., No. 9.

Researches on the Colouring-Matters derived from Triphenylmethane.—E. Noelting.—This seventh paper gives a description of the derivatives of triphenyl-

methane, obtained by the condensation of tetramethyldiamidobenzhydrol with the para-substituted amines.

Constitution of Oils for Alizarin Reds.—Paul Juillard.—The industrial analysis of these oils is generally confined to the determination of the fatty bodies. But it would be preferable to determine also the sulphuric acid and the glycerin, and to determine the molecular weights of the fatty bodies of the soluble and of the insoluble portions. Care must be taken in decomposing the oil that the soluble portion is at the outset of the analysis completely dissolved in the water, otherwise the numbers obtained are too high. The determination of the sulphur in the state of barium sulphate is the only admissible method. The determination of the soluble and the insoluble portions by the successive use of litmus and phenolphthalein leads only to erroneous results.

Molecular Organic Reactions obtained by Fusion.—Leo Vignon.—In all the cases examined the fusion-points observed differ from those calculated. In some bodies the melting-points observed are lower than those calculated, sometimes even below that of the most fusible component. In other instances they are slightly higher. The chemical functions of the bodies do not seem to have any influence on these results.

New Procedure for the Detection of Carbon Monoxide in the Blood.—H. Bertin-Sans and J. Moitessier.—This paper requires the accompanying figure of the apparatus required.

Series 3, Vol. vi., No. 10.

New Method for the Purification of Yeast.—J. Effront.—The author finds that bacteria in yeasts and worts may be destroyed by the addition of fluorides, 30—50 m.grms. to 100 c.c. of the liquid, though their spores are more resistant. By considerable doses of fluorides it is possible to destroy the spores of such ferments without interfering with the ulterior activity of the yeast.

Action of Isobutyl Iodide upon pure Trimethylamine in an Aqueous Solution in Equimolecular Proportions at Common Temperatures, and at 100°. Trimethylisobutylammonium.—H. and A. Malbot.—We may arrive at a quaternary ammonium with isobutyl iodide, on condition of placing it in presence of an amine which is sufficiently energetic. If the combination of isobutyl iodide with tri-isobutylamine is not effected the reason lies in the too feeble affinity of the amine for the ether.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Medical, 8.30.
TUESDAY, 12th.—Society of Arts, 4.30. "The Laos States of Upper Siam," by Ernest Satow, C.M.G.
—— Royal Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.
WEDNESDAY, 13th.—Society of Arts, 7. "Three States of Matter: Solid, Liquid, and Gaseous," by Prof. John M. Thomson.
THURSDAY, 13th.—Royal, 4.30.
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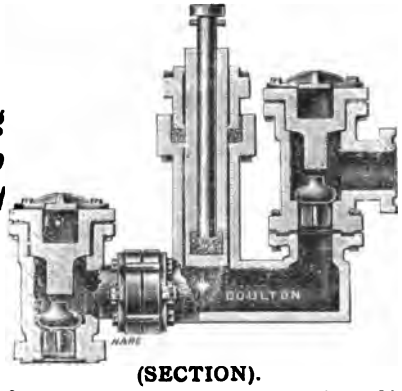

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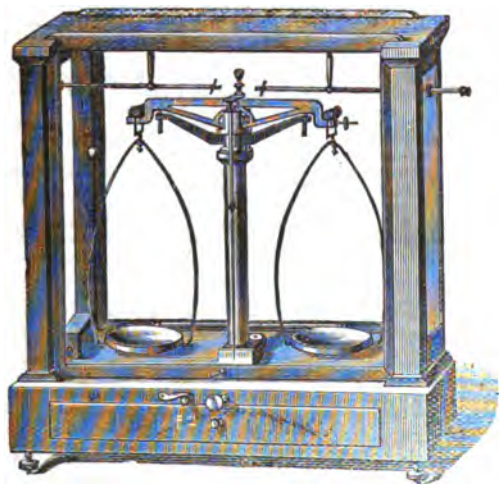

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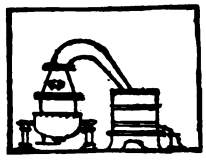

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THE CHEMICAL NEWS.

VOL. LXV., No. 1676.

A RAPID METHOD OF DETERMINING THE COMPOSITION OF LUBRICATING OILS.

By HAROLD GRIPPER, F.C.S.

THE great majority of the oils now used for machine-lubricating are mixtures of hydrocarbon and saponifiable oils. The existing methods for the determination of these constituents are accurate and easily worked, but somewhat tedious, all consisting in saponification and subsequent separation by extraction of the hydrocarbons with ether. The usual process (described in Allen's "Commercial Organic Analysis," vol. ii., p. 83) involves saponification, evaporation of the alcohol, dilution with water and cooling, separation in a separating funnel with ether, and finally evaporation of the ethereal layer and weighing of the residue. All this takes time, even if the separation in the separating funnel takes place rapidly, which is not always the case.

The following process I have found useful when a number of samples have to be examined at the same time, and when results approximately correct only are required, as is often the case in this laboratory. The results obtained are within 2 or 3 per cent of the truth. The method is simply an extension of the well-known Kœttstorfer process. 2½ grms. of the sample are saponified in the usual way with 25 c.c. of a solution of alcoholic potash about N/3 (with oils containing more than 50 per cent of saponifiable oil the usual N/2 strength may be used). When saponification is complete the titration is made in the ordinary way with N/2 HCl, using phenolphthalein as indicator, and a blank experiment having been made to estimate the strength of the alcoholic potash used, the percentage of KHO used by the sample is calculated.

The saponifiable oils chiefly used in the making of mixtures for lubricating purposes are—

	KHO absorption.	Saponification equivalent.
Brown cotton-seed ..	22·27 per cent.	252
„ rape	20·03 „	280
Neatsfoot	18·70 „	300
Lard	19·30 „	290
Tallow		
Castor	17·90 „	313

The potash absorptions therefore vary between 17·90 per cent and 22·27 per cent. It is necessary to take the mean of these figures (20·08 per cent) as the potash absorption of the unknown mixture of saponifiable matter in a lubricating oil. Then 100·0/20·08 = 4·98 parts of the oil are saponifiable by 1 part of KHO. Therefore if the percentage of KHO absorbed by the sample be multiplied by 4·98, the amount of saponifiable matter present will be obtained. Or the calculation may be simplified by multiplying the number of c.c. of N/2 HCl (corresponding to KHO neutralised) by (0·02805 × 40 × 4·98) = 5·587. The proportion of saponifiable oils is thus obtained. The amount of hydrocarbon oil is ascertained by difference.

But it is necessary to know the specific gravity of the hydrocarbon oils. In order to estimate this, the liquid in the oil flask is, immediately after titration, raised again to the boiling-point, and poured through a filter paper which has been saturated with boiling water. The alcoholic solution of soap and KCl will run through in two or three minutes, the hydrocarbon oils remaining on the filter. They are washed once with boiling water, and the specific gravity may then be taken by Hager's method. It is not necessary to wash the oil more than once, since in making Hager's test the globule of oil dropped into the alcoholic liquid is immediately cleansed thereby from all impurities. The specific gravity of the hydrocarbon oils and of the original mixture being known, the specific gravity of the saponifiable oils may be calculated by difference.

By this method an analysis may be completed, including the calculation of results, within an hour of the commencement of the saponification, and in examining a series it is of great advantage, a dozen samples being easily completed in a day. The only source of error is in the fact that the nature of the saponifiable oil, and therefore its exact saponification equivalent, is unknown.

	By titration.	By separation and weighing.
I.	78·3 per cent of hydrocarbon oil, sp. gr. 0·891 21·7 „ saponifiable oil, „ 0·950	
	79·4 per cent of hydrocarbon oil, sp. gr. 0·891 20·6 „ saponifiable oil, „ 0·955	79·3 per cent of hydrocarbon oil, sp. gr. 0·890 20·7 „ saponifiable oil, „ 0·957
	78·3 per cent of hydrocarbon oil, sp. gr. 0·891 21·7 „ saponifiable oil, „ 0·950	
II.	72·7 per cent of hydrocarbon oil, sp. gr. 0·900 27·3 „ saponifiable oil, „ 0·973	74·4 per cent of hydrocarbon oil, sp. gr. 0·900 25·6 „ saponifiable oil, „ 0·979
III.	76·6 per cent of hydrocarbon oil, sp. gr. 0·882 23·4 „ saponifiable oil, „ 0·956	76·7 per cent of hydrocarbon oil, sp. gr. 0·883 23·3 „ saponifiable oil, „ 0·953
IV.	65·4 per cent of hydrocarbon oil, sp. gr. 0·887 34·6 „ saponifiable oil, „ 0·966	64·1 per cent of hydrocarbon oil, sp. gr. 0·886 35·9 „ saponifiable oil, „ 0·964
V.	79·9 per cent of hydrocarbon oil, sp. gr. 0·885 20·1 „ saponifiable oil, „ 0·963	
	79·6 per cent of hydrocarbon oil, sp. gr. 0·885 20·4 „ saponifiable oil, „ 0·962	79·8 per cent of hydrocarbon oil, sp. gr. 0·886 20·2 „ saponifiable oil, „ 0·959
	79·9 per cent of hydrocarbon oil, sp. gr. 0·885 20·1 „ saponifiable oil, „ 0·963	
VI.	56·5 per cent of hydrocarbon oil, sp. gr. 0·906 43·5 „ saponifiable oil, „ 0·966	58·1 per cent of hydrocarbon oil, sp. gr. 0·908 41·9 „ saponifiable oil, „ 0·965

The accompanying results were obtained by the process described, and by the usually accepted method of separation with ether and weighing the hydrocarbons. The results are in all cases in approximate and in some cases in close agreement.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 21).

As on the large scale, *e.g.*, in the liver biliary capillary ducts, without walls run among the cells we must here conceive that on the small scale, in the cells themselves, there are capillaries, devoid of walls, which are connected with each other and mediate the exchange of the assimilable matters with the soluble constituents of the cellular body. The cellular membrane, and in its default the mutable surface of the protoplasm, necessarily modified by contact with the surrounding medium, exerts a purely physical elective influence upon the matters which enter or which come forth. If it were otherwise, all ova which are developed in water must perish, and the known laws of osmose would be inapplicable, for which we have no evidence. It is rather probable that in every protoplasmic tissue a certain class of substances is drawn in through the most superficial layer or skin in order thus to arrive in the protoplasmic capillaries, and ultimately to occasion distension, turgor, &c., whilst a certain number of substances which have been chemically modified in the internal spaces are prevented from escaping, so that growth and multiplication by the division of the superfluous nutriment is the necessary result; since the increase of mass occasioned by such intussusception, imbibition, and assimilation above a certain limit must cease; the condition for the individual processes, smallness of the entire space, and hence the absence of the action of mass.

The researches of W. Pfeffer on the membranes of the plasma, the vacuoles, the aggregate condition of the plasma, and on the osmotic processes in it, as well as a number of details observed by the best microscopists, supply our view with powerful supports.

But the necessity of capillary spaces in the protoplasm itself, for the occurrence of its entire chemism, has hitherto not been brought into prominence. These spaces are the seat of the fundamental chemical vital processes, the formation of carbon dioxide, of albumen, and of the consumption of oxygen. The currents which exist in every protoplasm as long as it lives, must be occasioned chiefly by the differences of pressure in the individual reactions. The osmotic pressure in the plasma may reach several atmospheres, whilst the counter pressure scarcely exceeds one.

It is therefore, at least, a highly probable hypothesis if we assume as the necessary foundation for all protoplasmic chemical activity, and, consequently for all vital processes, the constant presence of capillary spaces in every protoplasm, as in them the action of masses cannot be reached, and the single actions must accumulate.

Important as the cellular nucleus demonstrably is in many cases for metabolism, the idea of its being indispensable for the course of the processes of metabolism is refuted by the accumulated observations made on non-nucleated parts. In particular, the process of growth can no longer be referred to a function of the activity of the nucleus or of the cellular membrane. On the other hand, both are without question of the greatest influence in the maintenance of a certain kind of chemism in the capillary spaces. Even in the simplest osmotic pressures through a single thin membrane, the nature of such membrane, the temperature, the concentration of the solutions, and an entire series of physical conditions, have a determining action upon the final result. If then, nucleus and membrane have derived certain permanent properties by the combination of adaptation and inheritance, we can well conceive that they both signify more as regulators for the progress of the assimilation and dissimilation of the protoplasm than as regulators; when both are wanting, metabolism and differentiation are not regulated. But the more one or the other part has become morphologically individualised by being accustomed always to the same external conditions, the same saline solutions, temperatures, degrees of pressure, &c., the more such a tissue loses its plasticity, and then in its internal spaces the individual chemical reactions must ensue, more and more in a certain direction rather than in any other, so that the capacity for adaptation becomes smaller and smaller and is finally lost. In its place comes the specific energy. But in every organism there remains so much protoplasm not specifically differentiated, which remains fit for every function in the leucocytes, and in the sexual secretions, that the protoplasm, even here, may be regarded as a kind of microcosm, in as far as it produces an immeasurable variety of forms, and thus maintains in action the incomprehensibly differentiated life on the surface of the earth.

(To be continued).

SEPARATION OF BISMUTH AND LEAD.

By W. REMMLER.

The volatility of bismuth chloride as contrasted with lead chloride has previously been utilised for the separation of the two metals. Rose and Fresenius report on this separation, Vogel (*Zeit. f. Analyt. Chemie*, xiii., 61) considers the most suitable temperature for the separation to be 360° to 370°. He remarks that the mixture must not be heated too strongly, as otherwise lead chloride may be driven off; whilst if the temperature is too low, bismuth chloride may be left behind. As it is difficult to hit the right temperature, the author, at the instigation of Prof. V. Meyer, attempted the separation by heating in the vapour of boiling sulphur, and has found that this method allows an easy and accurate separation. As a first experiment, he heated lead chloride in the sulphur bath to ascertain if it sublimed at the temperature of boiling sulphur, since Vogel states that lead chloride is volatilised at 400°. He constructed an apparatus which he used for the following separations:—In a test-tube, 20 c.m. in length, and 3—4 c.m. in diameter, there are placed about 20 grms. of sulphur. Into this tube there projects downwards a second narrower tube, about 16 c.m. in length, fixed above in a cork, which at the same time serves as a loosely fitting stopper for the wider tube. A smaller glass (a test-tube of 4 c.m. in length) containing the substance to be analysed, is let down into the bottom of the second tube by means of a glass rod bent at its lower end into the shape of a ring, and thus supporting the smaller tube. During the heating, which lasts an hour, a current of dry chlorine is passed down into the innermost glass.

			Per cent.
0·5004 lead chloride lost in weight	0·0008 grm.	=	0·0159
0·5108 ,, ,,	0·0006 ,,	=	0·0117
0·5054 ,, ,,	0·0013 ,,	=	0·025

These losses are so slight as to have no influence upon the result of the analysis.

It was also important to ascertain if bismuth chloride is quickly and completely volatilised in the sulphur-bath. To this end, I placed in the wider glass, along with a weighed quantity of lead chloride, a weighed quantity of bismuth sulphide, and heated it in the sulphur-bath whilst chlorine gas was introduced as before.

After the lapse of an hour, he weighed the small glass and found that the mixture had lost weight to the amount of the bismuth sulphide present, whence it followed that at this temperature bismuth chloride was completely

volatilised. As in an analysis the metals to be separated are generally in the form of sulphides, it was necessary to determine whether lead sulphide is entirely converted into lead chloride in a current of chlorine. A weighed quantity of lead sulphide was treated in the same manner, when it was soon found by the change in the weight that the lead sulphide was not completely converted into chloride, but that the mass was melted together and was only superficially attacked by the chlorine. It was therefore probable that the lead sulphide would be converted better at a lower temperature, as it was proved by experiment. The lead sulphide was first boiled for an hour in the xylol-boiler, and then heated for an hour in the sulphur-bath in a current of chlorine. After the heating in the xylol-boiler the weight of the lead sulphide =0·2293 grm., increased by 0·0268 grm. If the conversion had been complete, the increase would have been 0·0374. The deficiency in weight of 0·0106 grm. was made up after heating for one hour in the sulphur bath; consequently, the sulphide was in this manner completely converted into chloride.

The attempt was now made to separate the two sulphides in this manner, heating first for an hour in the xylol-boiler, and then for another hour in the sulphur-bath. In a mixture containing 42·17 per cent of lead, there were found 42·09 per cent.

The result shows that the metals may be perfectly separated in this manner. — *Berichte Deutsch. Chem. Gesellschaft*, xxiv., No. 18, p. 3554.

ON THE FORMATION OF MAGENTA.

By B. GOLDBERG.

In a memoir on the influence of thiophene upon the colouration of the benzene derivatives, which appeared in the *Comptes Rendus* (cviii., 520), M. A. Bidet communicated the very remarkable observation that the mixture of perfectly pure bases (aniline, ortho-, and para-toluidine) free from thiophene, on heating with arsenic acid yielded mere traces of magenta; whilst the bases obtained from nitro-compounds, to which some thiophene had been added prior to reduction, yielded the same coloured mass as the ordinary aniline oil from reds.

Hence the formation of magenta would depend on the presence of thiophene derivatives, although in minimum quantities, which introduce the reaction, whether by an action of contact or in some other inexplicable mannner. There were, however, serious difficulties in the way of Bidet's observation, since, according to the observations of V. Meyer, amido-thiophene is a very unstable body, which is resinified in a short time at common temperatures, and which therefore cannot possibly be present in commercial aniline, even if it had been prepared from a material rich in thiophene. That commercial aniline is, in fact, free from amido-thiophene is confirmed by its conversion into benzol free from thiophene by the process of diazotising. The nitro-thiophene added would therefore be destroyed on reduction and subsequent distillation, and could therefore exert no influence upon the reaction of the formation of magenta. Hence, a repetition of Bidet's experiments seemed interesting. This task was undertaken by the author at the request of Prof. V. Meyer. The pure bases were first obtained by Bidet's process from nitro-benzol and para-nitro-toluol, which had been freed from nitro-thiophene by repeated treatment with concentrated sulphuric acid; and secondly, from benzol and toluol free from thiophene.

1. Nitro-benzol and nitro-toluol were treated with concentrated sulphuric acid at a gentle heat until the sulphuric acid added no longer changed its colour, or until a specimen on treatment with alcoholic potassa no longer gave the very characteristic reaction of dinitrothiophene, and was then reduced in the ordinary manner. The bases were then twice fractionated, those from aniline being collected at 184°, and those from para-toluidine at 197°. The mixture, when heated with mercuric chloride, yielded at once an intense violet-red melt, which was also obtained on heating with arsenic acid.

2. In order to be quite certain that the colouration, in view of the intense tinctorial power of magenta, was not due to traces of this body formed in its midst, the following experiment was performed, for which the bases were derived from pure benzol free from thiophene, and from toluol freed from thiophenes by repeated treatment with concentrated sulphuric acid. From the pure bases there was prepared a mixture of 2 mols. aniline, and 1 mol. para-toluidine; and of this, 0·9894 grm. heated in the oil-bath for one and a half hours to 180—200° along with 2·8 grms. mercuric chloride and 2 grms. (excess) of aniline. Simultaneously with this experiment, 0·9740 grm. of a similar mixture of the commercial bases were likewise treated in the same manner along with 2·8 grms. mercuric chloride and 2 grms. commercial aniline in excess. In each case there was obtained a splendid violet-red melt. Each melt was extracted with 100 c.c. of alcohol, and in each case a solution of a deep red colour was obtained. The better to compare the tones, $\frac{1}{10}$ c.c. of each solution was diluted with 100 c.c. of alcohol. Both were almost identical, that from the pure bases having the purer tone.

After these experiments, Bidet's statement may be regarded as erroneous.

For experiments on a small scale, the process of preparing magenta by heating with the calculated quantity of mercuric chloride in presence of an excess of aniline may be strongly recommended. It yields scarcely any carbonaceous amorphous substances, which cannot be avoided in the arsenic acid, &c., methods. — *Berichte Deutsch. Chem. Gesellschaft*, xxiv., No. 18, p. 3552.

ON THE STABILITY OF THE PETROLEUM COMPOUNDS.

By H. N. WARREN, Research Analyst.

The alkaline cyanides of potassium and sodium, regarded as organic compounds, may deserve rank among the stable compounds, insomuch that they exist unchanged at temperatures that would speedily disintegrate all other organic compounds. But of all organic compounds none can be said to possess more tenacity than the hydrocarbons petroleum, paraffin, &c., which, whether existing in the liquid or solid condition are simply changed upon elevation of temperature into a more gaseous compound, retaining their former properties. For instance, if petroleum, boiling at a low temperature, be passed through heated tubes, it becomes fractionised into compounds boiling at temperatures in accordance with the temperature to which it has been subjected, until a red heat is reached, when a true gaseous hydrocarbon is obtained, burning with the ordinary luminosity of these compounds and capable of reducing certain metallic oxides when brought in contact with it at an elevated temperature, at the same time forming substitutional compounds with the elements bromine, chlorine, &c. Strange to say, the hydrocarbons of the following class, although somewhat readily changed by heat, further resist most stubbornly the most powerful oxidising agents. Few, if any compounds, can resist the oxidising influence of fused nitre, yet petroleum may be passed through this substance with impunity even when at a bright red heat, and collected unchanged. The liquid or more solid compounds, if heated in sealed tubes with fuming nitric acid, are practically unchanged; an instance of this may be recorded from the bursting of an iron tube containing the mixture that had been kept for four hours at a temperature of 600° F.; small quantities collected afterwards possessed all their former properties. The only oxidising agent of sufficient power is chlorochromic

acid; if a few c.c. of this substance be allowed to fall to the bottom of an ounce of water, at the same time a layer of petroleum be brought to play upon the surface, on now shaking the whole briskly, a most energetic action is at once apparent, the petroleum becoming changed into a semi wax-like substance melting at about 400° F. This substance has, as yet, not been sufficiently dealt with to ascribe to it a formula, but it is the author's intention to deal further with the compound when time permits.

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ON THE

DETERMINATION OF THE MELTING POINTS OF MINERALS.*

Part I.—The Uses of the Meldometer.

By J. JOLY, M.A., D.Sc., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

(Continued from p. 18).

It is necessary before proceeding further to describe the form of meldometer used in determining melting-points in the manner just sketched out. The accompanying figure (Fig. 2) from a photograph shows the apparatus (made by Messrs. Yeates and Son) at present in use. It consists of a rectangular piece of slate, cut into the form shown, on which two forceps are affixed, one rigidly (the further one on the figure), the other so that it is free to rotate round a vertical axis at one extremity, beyond which it is prolonged by a fine flat spring of steel. When these forceps are parallel to one another the distance separating their jaws is closely 10 c.m. This is the length of platinum ribbon whose expansion is measured when making experiments. A small helical spring attached to the vertical axle of the movable forceps, and to the fixed piece which receives the upper pivot of this axle (this piece conceals it in the figure), serves to confer a *slight* tension on the platinum ribbon, in that it is set to turn the forceps clockwise on its axis. Thus, when the ribbon expands the forceps rotates a little clockwise. At the further extremity of the spring which prolongs this forceps, a small polished plate of gold is attached, and to meet the surface of this a gold wire, carried at the extremity of the micrometer screw seen on the figure, may be brought on advancing the screw. The point of contact of pin and plate is as nearly as possible at the same distance to the one side of the vertical axis of the forceps as the centre line of the ribbon is to the other, when the latter is in its proper position in the forceps. Thus, the expansion of the ribbon may be measured by the movement of the micrometer screw, if at each change of temperature we get the gold pin to touch the gold plate *exactly*. To effect this without troublesome observations matters are arranged so that the meeting of pin and plate closes a circuit in which a galvanometer and a Leclanchè cell are included. The bed of slate insulates the screw and forceps, and connexions are made as on the diagram (Fig. 3). This is an extremely sensitive method of reading a small movement. The screw pitch is about the fourth of a m.m.; the micrometer head carries 100 parts. Half these last divisions may easily be read, that is to say, the $\frac{1}{800}$th of a m.m., or less than the $\frac{1}{20000}$th of an inch, a quantity approaching the limits of the highest powers of the microscope, and indeed little more than two wave-lengths of sodium light. This movement is equivalent to a change of temperature of about 1·5° centigrade. The micrometer screw must have a uniform thread and be reliable in its readings, or error will, of course, be introduced, just as would be the case with a badly calibrated thermometer. To bring the current into the forceps two large binding screws (seen in Fig. 2) are provided. These are attached to copper straps passing beneath the slate bed, and communicate with the forceps. To insure good contact with the movable forceps an annular space around the axle is provided in the slate, into which a little mercury can be

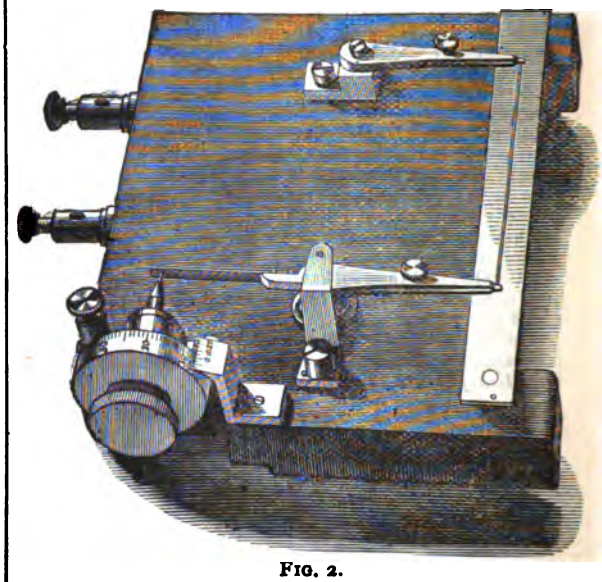

Fig. 2.

poured. A perforated wooden lid, loosely encircling the axle, keeps this mercury from accidentally being spilled out. The bottom of the mercury well is of brass, which receives the pivot of the axle on its upper surface, and at its under surface is screwed to the copper conductor. The forceps close by their elasticity, and are opened for the insertion of the ribbon by the small screws seen in the figure. A slip of polished brass, passing beneath the

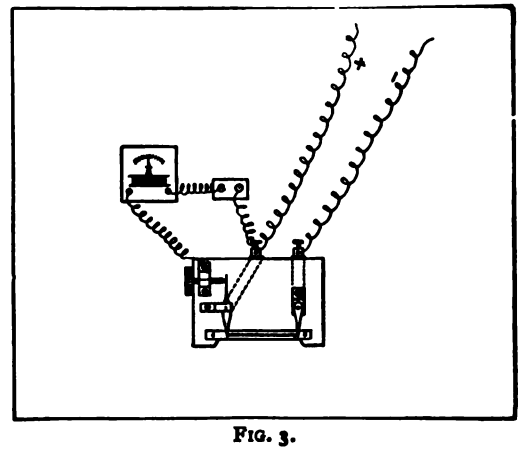

Fig. 3.

ribbon, serves to intercept heat from reaching the edge of the slate, and to receive chance fragments of substances falling off the platinum. The slate is cut back beneath this, for it is an object in the construction of this apparatus to preserve the slate from change of temperature. There seems but little heat communicated to the slate. I have not detected any sensible heating, even after prolonged experiments at high temperature. The co-

* A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

efficient of expansion of slate is so small that but little error can, I think, creep in in this way.

The platinum ribbon used in this apparatus is similar to that used in the first described form of the meldometer. The resistance of 10 c.m. of the ribbon, cold, is 0·43 ohm; when hot, rising to 1·5 ohms. A current of 6 ampères raises this length of ribbon to its melting-point. The ribbon is cut away at each end where fixed in the forceps, so that its section is reduced considerably where meeting the cold metal of the forceps. This adjustment is very important in this form of the meldometer. Any serious loss of heat by conduction from the ends of the strip produces an effect increasing with the temperature, not in a simple ratio, but more as the square of the temperature, the electrical

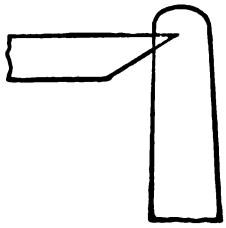

FIG. 4.

resistance being affected by the fall in temperature in such a way as to intensify the effect. Thus, the curve found for the extension will be affected; the curvature will tend generally to be diminished at high temperatures, and the position upon the ribbon we assign to the standard substances will also enter as a factor, for there will be inequality of temperature along the ribbon. A reduction of section to about one-fifth the full section will bring up the temperature at the ends sufficiently to reduce the error to a very small amount. It is easy to see, at a full red heat, how far the tint is uniform up to the forceps; but a more exact test may be made by reading melting-points within about 12 m.m. from the ends and at the middle, which should afford a difference not exceeding 5° C. at a dull red heat. It will be found

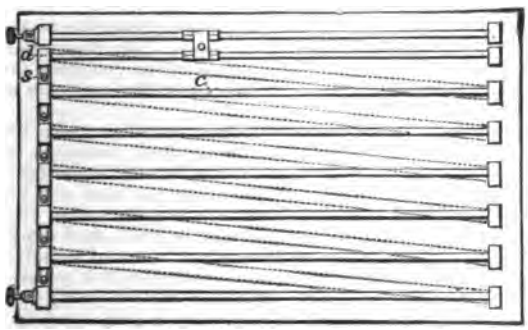

FIG. 5.

that if the ribbon be cut away with a scissors, and clamped as in figure 4, there will be sensible uniformity of temperature over the central 6 c.c. of the ribbon. I may observe that sometimes in the case of a ribbon very much cut away, and with a particular tension of the spring, keeping it stretched, a transverse vibratory motion of the ribbon takes place when it is heated. This is due apparently to air currents in the same manner as a flat body thrown into the air falls, with horizontal oscillations, from side to side. This vibratory motion, of course, renders vision indistinct. It may be stopped by bringing a fine platinum wire, fixed to a support, to touch the edge of the ribbon at its central point, but I have only occasionally noticed the phenomenon.

Before using a particular ribbon for measurements all traces of kink or bend are got out of it by raising it to a white heat for half a minute. In this connection it must be mentioned that the pull on the ribbon must be very slight, just sufficient to keep it stretched. A force equivalent to the weight of 1·5 grms. is sufficient. The ribbon I have found it best to use weighs 0·0073 grm. per c.m. run. The maker's number for this is 0·170. A less section is not advisable, as being too much affected by slight draughts. It is essential, of course, that the ribbon be of constant cross-section. There is some advantage in surrounding the ribbon by an open trough-shaped box of platinum foil from end to end. But while this conduces to steadiness in the temperature of the strip, it has the disadvantage of introducing a fresh difference of conditions towards the ends, except troublesome arrangements are made.* On the other hand, the amount of fluctuation obtaining in the case of observations made in a quiet room are small, and often not disadvantageous in observing the melting-point. Thus we observe the condition of the substance changing with these small fluctuations; and we set the micrometer so that the galvanometer needle is free when the substance shows the first signs of melting, and is deflected on the instant that solidification takes place. In this way the melting-points of non-viscous bodies can be caught with much accuracy. And I may observe here that, although some of Carnelley's observations (*Jour. Chem. Soc.*, vol. i., 1876) appeared to indicate a considerable difference between the melting-point and the solidifying-point of many of the salts he dealt with, this difference is not substantiated by observations on the meldometer. The salt may generally be observed, with care, in such a state that the zone of liquefaction may be seen advancing from beneath, or retreating downwards at the least fluctuation of temperature. I think the method adopted by Carnelley for determining the point of the solidification was calculated to introduce an error due to radiation.

It is advisable not to assume that a curve plotted for one ribbon is suitable to another one which has replaced it, till we have verified a couple of points upon it, using such easily observed melting-points as are given in the sequel. Thus, if a speck of silver chloride, and of the black oxide of copper, CuO, be melted upon it, and finally a little palladium, we may assure ourselves upon this point. To avoid any chance of error due to the position of the substance upon the ribbon, no more than the central 6 c.m. should be availed of for determinations.

For the control of the temperature a higher resistance than that previously described is necessary. As the Rheostat I have in use is new in many particulars, and is very satisfactory, I think it well to describe it. It consists (Fig. 5) of eight rods of carbon, having a total resistance of about 4 ohms, fixed horizontally upon a board. Two of these are provided with a sliding cross-connection; the others may be, one by one, thrown into circuit, or cut out by a few turns of the screws seen at the front of the board in fig. 5. The raising of one of these screws, for example, permits a brass plate to spring out of contact with the underlying metal, and as the plate is cut out sufficiently to clear it of the shaft of the screw, connection is broken when the nut is raised, till it is no longer followed by the plate. The current then must traverse the carbon *c*, returning to the point *d* by the dotted connection. It is evidently possible to secure a perfect gradation of temperature by the use of this resistance, the travel of the bridge commanding a greater resistance than that of a single carbon. Thus if, when a certain number of carbons are in circuit, and the bridge has been moved to cut out the entire length of the two bridged carbons, we need still a higher temperature, we restore the bridged carbons to circuit by moving back the bridge, and then cut out one of the carbons, after which we begin again to advance the bridge so as gradually to cut out

* I have lately got over this difficulty, and the instrument as at present made is provided with a covering for the ribbon.

the bridged carbons. In this way we increase the temperature, nor is it necessary to take our attention from the microscope and the manipulations of the micrometer while making these changes in the resistance.

The diagram (Fig. 3) shows the convenient disposition of the apparatus when effecting measurements; the adjustable resistance being supposed inserted in the right hand lead. To observe the objects upon the ribbon a simple form of microscope, mounted on a bracket, projecting from a heavy base, is requisite. This can be moved along and directed to any point of the ribbon. One ribbon, of course, serves for many observations.

A principal advantage of this electrical method of reading the elongation of the ribbon is contained in the fact that so little of the observer's attention is called upon to effect this ordinarily difficult measurement. This is very important, for slight variations of temperature are continually occurring, due to draughts chiefly, and it is essential to be able to seize the reading at the moment the substance melts, especially in the case of bodies which flood out suddenly upon the platinum. The galvanometer needle may be observed simultaneously, with the object in the field of the microscope, if the head be raised a little above the eye-piece. The left hand is kept upon the micrometer screw, and at each small movement of the bridge (effected by the right hand), the elongation is followed by the micrometer, and the behaviour of the substance at the increased temperature observed.

(To be continued).

THE DETECTION AND DETERMINATION OF POTASSIUM SPECTROSCOPICALLY.*

By F. A. GOOCH and T. S. HART.

(Concluded from p. 24).

EXPERIMENT III. was made to discover the effect of the presence of a reasonable amount of sodium chloride upon the determination of the potassium. To a portion of the solution if pure potassium chloride containing 0·01 grm. of the element was added 0·1 grm. of sodium chloride taken from the salt purified as previously described. This solution was diluted and the comparison made with the standard according to the accompanying account.

Experiment III.

Volume of the test solution.	Characteristic of line compared with standard.
25 c.m.³	stronger
50 ,,	,,
80 ,,	,,
90 ,,	,,
95 ,,	,,
105 ,,	,,
120 ,,	like

(120 × 0·0001 = 0·0120)

Potassium found	0·0120 grm.
,, taken	0·0100 ,,
Error	0·0020 ,,

The result of this experiment was most surprising; for, instead of diminishing the delicacy of the test, we find that the presence of a moderate amount of sodium chloride tends to increase the brilliance of the potassium line. The sodium chloride employed was a part of that prepared and tested as previously described and used in the experiments upon the qualitative determination of potassium. By no possibility could the 0·1 grm. of it taken in the experiment have contained more than 0·000001 grm. of potassium. It is evident, therefore, that the brilliance of the potassium line gained 20 per cent in strength by the influence of sodium chloride, amounting to ten times the weight of the potassium present when the effect due to impurity of the salt could by no means exceed a hundredth of 1 per cent; that is to say, the observed effect is, at the very least, two thousaud times greater than that which might have been conceivably produced by contamination of the sodium salt.

In the following experiment the effect of varying amounts of sodium chloride upon the spectrum of the potassium is shown. The sodium line was turned out of the field of view to obviate the dazzling effect of the sodium light, and a solution of potassium chloride containing 0·01 grm. of the element in 100 c.m.³ was examined spectroscopically after the addition of successively increasing amounts of sodium chloride, the strength of the line observed being brought into comparison with that produced by similar portions of the potassium solution containing no sodium.

Sodium chloride in a coil-full. M.grm.	Potassium in a coil-full. M.grm.	Ratio of NaCl : K.	Width of slit. M.m.	Characteristic of line compared with standard containing no NaCl.
0·002	0·002	1 : 1	0·18	like
0·010	0·002	5 : 1	0·18	,,
0·020	0·002	10 : 1	0·18	a little stronger
0·040	0·002	20 : 1	0·23	much stronger
0·200	0·002	100 : 1	0·23	very much stronger
0·400	0·002	200 : 1	0·23	much stronger
0·600	0·002	300 : 1	0·23	,,

From this it appears that the maximum strengthening effect occurs when the sodium chloride stands to the potassium in the ratio of 100 : 1. The apparent diminution of brilliance when the sodium is increased beyond that proportion is doubtless due to the effect of the strong light diffused through the field of view by the intensely bright sodium flame in spite of the fact that the line itself is cut off from direct vision.

The cause of the brightening effect of the sodium chloride we are inclined to attribute to the chemical action of the sodium dissociated in the flame. The effect of ammonium chloride, and of hydrochloric acid, in destroying the potassium light is well-known, and is due, presumably, in very large degree to the prevention of the dissociation of the potassium chloride. The dissociated sodium should naturally by its mass-action reinforce the disintegrating action of the heat upon the molecule of potassium chloride.

It is plain that the complication introduced into the quantitative spectroscopic determination of potassium by the presence of the sodium salt in the test can be obviated if it can be brought about that both the test and the standard solution shall contain the same amount of that reagent. It is a matter of interest, therefore, to discover whether it is possible to match sodium lines of considerable intensity so closely that the quantities of that element in solutions brought into comparison shall be practically equal, and so may be relied upon to give the same strengthening effect to the potassium spectrum. The following statement is the record of an attempt in this direction. The narrower slit was found to be best adapted to the comparison of the sodium lines.

NaCl in a coil full of new solution.	NaCl in a coil full of standard.	Width of slit.	Characteristic of line as compared with that of standard.
0·010 m.grm.	0·02 m.grm.	0·18 m.m.	weaker
0·017 ,,	0·02 ,,	0·18 ,,	weaker
0·019 ,,	0·02 ,,	0·18 ,,	weaker
0·020 ,,	0·02 ,,	0·18 ,,	like

The result shows the possibility of matching the sodium lines with a degree of approximation sufficient for the purpose in view; and, accordingly, a new standard solution was made containing 0·01 grm. of potassium taken

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlii., December, 1891.

Experiment IV.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 c.m.³ of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
30 c.m.³	0·23 m.m.	stronger	0·01 grm.	0·18 m.m.	weaker	108 c.m.³ (*a*)	0·23 m.m.	weaker
70 ,,	0·23 ,,	,,	0·03 ,,	0·18 ,,	,,	108 ,,	0·23 ,,	stronger
100 ,,	0·23 ,,	weaker	0·05 ,,	0·18 ,,	,,			weaker
			0·08 ,,	0·18 ,,	,,	109 ,,	0·23 ,,	stronger
			0·09 ,,	0·18 ,,	,,			like
			0·10 ,,	0·18 ,,	like			

(*a*) The test-solution having been accidentally over-diluted, its strength was increased by the addition of 0·0010 grm. of potassium, and this amount was added in the computation below to that originally in the test-solution.

(109 × 0·0001 = 0·0109)

Potassium found	0·0109 grm.	
,, taken	0·0110 ,,	
Error	0·0001 ,,	= 0·9 per cent.

Experiment V.

Part I.			Part II.			Part III.		
40 c.m.³	0·23 m.m.	stronger	0·025 grm.	0·18 m.m.	weaker	160 c.m.³	0·23 m.m.	stronger
100 ,,	0·23 ,,	,,	0·050 ,,	0·18 ,,	,,	180 ,,	0·23 ,,	,,
160 ,,	0·23 ,,	weaker	0·085 ,,	0·18 ,,	,,	190 ,,	0·23 ,,	,,
			0·100 ,,	0·18 ,,	,,	200 ,,	0·23 ,,	,,
			0·110 ,,	0·18 ,,	like	205 ,,	0·23 ,,	weaker
						210 ,,	0·23 ,,	,,

(205 × 0·0001 = 0·0205 / 200 × 0·0001 = 0·0200} mean = 0·02025)

Potassium found	0·02025 grm.	
,, taken	0·02000 ,,	
Error	0·00025 ,,	= 1·25 per cent.

Experiment VI.

Part I.			Part II.			Part III.		
40 c.m.³	0·23 m.m.	stronger	0·045 grm. (*b*)	0·18 m.m.	weaker	110 c.m.³	0·23 m.m.	stronger
80 ,,	0·23 ,,	,,	0·082 ,,	0·18 ,,	like	120 ,,	0·23 ,,	,,
100 ,,	0·23 ,,	,,				130 ,,	0·23 ,,	like
110 ,,	0·23 ,,	like						

(*b*) Originally present.

(130 × 0·0001 = 0·0130)

Potassium found	0·0130 grm.	
,, taken	0·0140 ,,	
Error	0·0010 ,,	= 7 per cent.

Experiment VII.

Part I.			Part II.			Part III.		
						First.		
30 c.m.³	0·23 m.m.	stronger	0·05 grm. (*c*)	0·18 m.m.	weaker	100 c.m.³	0·23 m.m.	stronger
90 ,,	0·23 ,,	,,	0·07 ,,	0·80 ,,	,,	120 ,,	0·23 ,,	,,
100 ,,	0·23 ,,	weaker	0·09 ,,	0·18 ,,	,,	130 ,,	0·23 ,,	,,
		like	0·10 ,,	0·18 ,,	like	140 ,,	0·23 ,,	,,
					stronger			weaker
					,,			
						Second.		
						120 c.m.³	0·23 m.m.	stronger
						140 ,,	0·23 ,,	,,
						150 ,,	0·23 ,,	,,
								weaker
						160 ,,	0·23 ,,	,,

(*c*) Originally present.

First.

(140 × 0·0001 = 0·0140)

Potassium found	0·0180 grm.	
,, taken	0·0150 ,,	
Error	0·0010 ,,	= 7 per cent

Second.

(150 × 0·0001 = 0·0150)

0·0150
0·0150
0·0000

in the form of the chloride, and 0·1 grm. of sodium chloride in 100 c.m.³, and with this new standard the following determinations were made. The experiment was performed in three stages; first, the test solution was diluted until its potassium line matched approximately with that of the standard; secondly, sodium chloride was added to the solution thus diluted until the sodium lines were brought to equality; and, finally, the test solution and the standard were again brought into comparison.

From these results it is plain that the sodium in test and standard may be matched closely enough to allow a fair approximation to be made in the determination of the potassium. In Experiments IV., V., and VI., no readjustment of the percentage of sodium in the final dilution, subsequent to the matching of the sodium lines, was attempted; in Experiment VII. this point was looked to, so that in this determination the strength of the sodium was kept equal to that found in the matching process. In Experiments IV. and VII. the matching of the sodium in the test-solution against that in the standard proved to have been exact; in V. an excess of 10 per cent was added, and in VI. the point of equality was thought to have been reached while there was still a deficiency of 25 per cent in the sodium chloride of the test-solution.

The error in the determination of the potassium in Experiment VI. may, perhaps, be accounted for by the mistake in matching the sodium; that of the first attempt in Experiment VII. we are disposed to attribute to lack of care in keeping the eye of the observer in the most sensitive condition, and of attention to the point of bringing the wires to the plane in quick succession. The largest absolute error met with amounted to 1 m.grm. in a total of 15. Though not accurate to the last degree when large amounts of potassium are to be estimated, the method, we think, offers some advantage without too great sacrifice of exactness in the determination of small amounts. In qualitative work the mode of manipulating described is exceedingly satisfactory. Aside from the practical application of the method the point which has been of greatest interest to us is the development of the fact that the presence of sodium salts in the flame is of direct influence in strengthening the spectrum of potassium.

THE GREENWOOD PROCESS FOR THE DIRECT PRODUCTION OF CHLORINE AND CAUSTIC SODA.

On Wednesday, January 6th, we had the opportunity of inspecting this process, which is now being carried out in temporary works at Battersea. Mr. Greenwood, the inventor, has turned his attention to the electrolytic decomposition of common salt in connection with the extraction of gold from its ores by the chlorine process, and certainly, as far as we can judge from a necessarily brief examination, he has made a considerable step in the application of electric currents in industrial chemistry. The raw material operated upon is common salt, which is dissolved in water, and the brine, without any purification or filtration, is at once submitted to a current of about 4·4 volts and an intensity of 10 ampères per square foot of electrode.

The first difficulty to be overcome was to find a material for the anodes which should resist the action of nascent chlorine. The inventor has selected retort-coke, made up into plates and rendered impervious by a composition the nature of which is not made known. To increase the conductivity of the anode, and to give it greater firmness, it is provided with an iron core. This core is completely protected from contact with the chlorine by means of the composition just mentioned.

The next great difficulty is to prevent the chlorine and soda from re-combining. For this purpose, Mr. Greenwood has devised a peculiar diaphragm; it consists of slips of slate fixed horizontally like the laths of a Venetian blind, the interstices being filled with asbestos. If a mol. of chlorine impinges upon the slips, it could pass the diaphragm only by descending, and as its specific gravity is lower than that of the liquid, such a descent cannot take place.

The cathodes are made of cast iron, upon which caustic alkalies have practically no action. The liquid, after passing through a descending series of electrolytic troughs, is pumped back to be further submitted to the action of the current. The chlorine gas is at once conveyed away as liberated and passed into milk of lime, by which it is absorbed; or it may be applied to any other purpose as required. Thus it may be passed into lead chambers for the production of chloride of lime in the ordinary manner. This process being perfectly familiar to chemists is not shown in the experimental works now in action.

The caustic soda can, if needed, be converted into the solid form by evaporation, which is effected by the usual process. During this operation the common salt which has escaped decomposition—about 20 per cent, which would be very objectionable, *e.g.*, in the manufacture of soap—is eliminated by subsidence.

The production of caustic soda and of chlorine by this process is estimated by the inventor and by the experts who have been consulted to involve an economy of 50 per cent as compared with the present methods. If this calculation holds good on the large scale, and if no drawbacks reveal themselves, we may consider that the Leblanc alkali process is within a measurable distance of its end.

Mr. Greenwood has not as yet taken into consideration the question of the production of hydrochloric acid at a reduced cost. The cessation of the present supply of "tower salts" will be a serious affair in various chemical trades.

NOTICES OF BOOKS.

A Manual of Physics: Being an Introduction to the Study of Physical Science. Designed for the use of University Students. By W. Peddie, D.Sc., F.R.S.E., Assistant to the Professor of Natural Philosophy in the University of Edinburgh. Small 8vo., pp. 500. London: Baillière, Tindall, and Cox.

Dr. Peddie gives in his preface a very good *raison d'être* for his work. He admits the importance of studying distinct treatises on the various branches of physics, as written by the most eminent *savants* of the day. But he urges that the student who follows this plan too exclusively may fail to get a complete view of "the essential unity and interdependence" of all these branches as it is evidently desirable. Too many of our investigators are, indeed, so immersed in the study of details that they forfeit the *esprit d'ensemble*. To counteract this defect is the author's object.

We doubt, however, whether he sufficiently appreciates the distinction between science and art. Thus, in his first chapter he writes, "the *sciences* of navigation and ship-designing, of energy, mineralogy, geology, meteorology, and so on, are purely physical sciences." Now, we submit that navigation, ship-designing, engineering, are not sciences but arts; mineralogy, geology, meteorology, &c., are sciences, part and parcel of the interpretation of the cosmos. Art tells us what to *do* in order to produce certain results; science tells us what *is*.

Dr. Peddie very justly insists that we have only two methods for obtaining accurate knowledge,—*observation* and *experiment*. Yet, in face of this incontrovertible truth, there are many persons in Edinburgh and elsewhere who seek to prohibit experiment as far as living matter is concerned. The remarks on the practical work

ing of the inductive process, on hypotheses and theories, will prove invaluable to the true student.

The chapters on the theory of contours and its physical applications, and on varying quantities, treat of subjects too generally omitted in our ordinary text-books of physics.

In the chapter on matter we note two interesting dicta. We read that matter devoid of all energy "most probably would not be matter at all in the sense in which we use the word"; and again, we know of the existence in nature of only a comparatively small number of elements. Into the origin of the elements the author does not enter. The chapters dealing with heat, light, electricity, and magnetism are characterised by great clearness, and will form a sound basis for the special study of any one of these subjects. As a whole the work must be pronounced highly satisfactory, creditable to author and publishers, and calculated to be useful to the readers for whom it is intended.

The Principles of Chemistry. By D. Mendeléeff. Translated from the Russian (Fifth Edition) by George Kamonsky, A.R.S.M., of the Imperial Mint, St. Petersburg. Edited by A. J. Greenaway, F.I.C., Sub-Editor of the *Journal of the Chemical Society*. In Two Volumes, large 8vo., pp. 611 and 487. London: Longmans, Green, and Co.

We have not yet quite completed our survey of the German edition of Prof. Mendeléeff's great work, translated by L. Jawein and A. Thillot, now appearing in parts.

As a matter of course, the two versions are substantially identical. The English edition now before us does not contain—as the preface informs us—two notes referring to the meaning of Russian words, and a description of the water of the streams near Petersburg, of merely local interest. On the other hand, it is enriched with three important appendices. The first of these is a reproduction of Prof. Mendeléeff's lecture delivered at the Royal Institution of Great Britain, on May 31st, 1889, being "An Attempt to Apply to Chemistry one of the Principles of Newton's Natural Philosophy." The author, setting out from Newton's third law of motion, shows that it is possible to preserve to chemistry all the advantages arising from structural teaching without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The third Newtonian law is, in fact, the great principle of substitution which since the middle of the century has led to such triumphs in chemistry, and from which still higher results are to be expected.

Appendix II. has for its subject the "Periodic Law of the Chemical Elements," and is the "Faraday Lecture" delivered by Prof. Mendeléeff, on June 4th, 1889, before the Fellows of the Chemical Society. Here the illustrious Russian *savant* develops his polemical attitude towards the concept of a primary material or *protyle* and against the origin of the elements by a process of evolution. He urges that evidence, whether experimental or theoretical, is wanting. It is very true that we have never seen, *e.g.*, nickel converted into cobalt or *vice versâ*; but no more have we seen the zebra converted into the quagga. Both these animals are now concluded to have sprung, not the one from the other, but from an earlier less specialised type. Just so with the nickel and cobalt, or with other closely allied groups of elements.

As for theoretical or speculative evidence, the periodic law renders it impossible to conceive of any other manner in which the elements can have originated, unless we embrace—as Prof. Mendeléeff appears *not* to do—the idea of a distinct special creation for each.

Appendix III., taken from the *Journal of the Russian Physico-Chemical Society*, vol. xxii., 1890, No. 8, discusses the epochal discovery of Th. Curtius, the formation of hydro-nitrous acid, otherwise known as hydrogen nitride, azoimide, nitrohydric acid, N_3H. The possible existence of this compound Prof. Mendeléeff alleges that he had foreseen. For the composition of these bodies, N_3H and N_4H_4, he refers to "one of his unpublished notes, dated 1871 or 1872;" though he admits that the announcement is of less importance than if it had been made previous to the publication of the memoir of Curtius (*Berichte Deutsch. Chem. Gesellschaft*, xxiii., p. 3023).

The author's remarks on the part to be played in education by the study of science, and especially by that of chemistry, are admittedly opportune and suggestive. He tells us—and would our heads of colleges, &c., could feel the truth and the value of his words—that "we are compelled to cast aside classical illusions, and to engage in a work which not only gives mental satisfaction, but is also practically useful."

"Knowing how contented, free, and joyful is life in the realms of Science, one fervently wishes that many would enter their portals." But how different is the career of the student seeking to widen the domain of human knowledge from that of the victim seeking mainly to pass!

Says Prof. Mendeléeff: "The time has come to turn away from visionary contemplation, from platonic aspirations, and from classical verbosity, and to enter the regions of actual labour for the commonweal, and to prove that the study of science is not only an excellent education for youth, but that it instils the virtues of labour and truth."

We have no hesitation in saying that the present edition is much preferable to the version of Jawein and Thillot. We think no one ought to enter upon the philosophy of chemistry without having prepared himself by a careful study of the work before us.

CORRESPONDENCE.

PAYMENTS ON RESULTS.

To the Editor of the Chemical News.

Sir,—The changes which will be introduced into the scale of payments for science instruction by the Science and Art Department next year amount almost to a revolution; but while the scale of payment is to be completely changed, with a view, apparently, of cutting down the grant, the system on which the payments are based remains the same.

Surely the time for payments on results has now passed. Admitting that as a temporary expedient for giving a stimulus to science teaching, and enabling classes to be started in places where otherwise it would have been impossible, it was useful and served its purpose. Its time has now passed, and we have reached a condition when it has not only ceased to be useful, but has become highly injurious to the best interests of science.

In all large towns there are now organised science and technical schools, where instruction is given in science, and which depend to a large extent on the government grant for their income. The instruction in most of these institutions is good, but it might be made much better if the students had not all to be put through the examination mill in order to obtain grant.

The teaching in technical schools is therefore kept at a low level, and its efficiency much impaired by the system of payment on results. But this is not all. Any person holding a "first class advanced" certificate in any one subject of science may teach that subject, and no objection will be raised to his starting a class if he can get a committee formed. As a result, school teachers who hold a certificate very frequently start evening classes at their schools. In many towns the School Board provides the room, gas, and apparatus, and the teacher takes the grant. The teaching is often of the poorest description, and the classes are run at very low fees, lower than is

possible at the regularly organised schools, where the teachers are more highly qualified, and therefore have to receive fairly good salaries; and not unfrequently the teacher offers a prize to each student who passes the examinations, that is, he gives the student a proportion of the grant earned. Young men commencing a study of science do not know the difference; to them "certificated science teacher" seems quite sufficient qualification, and the low fee is an inducement, so they too often go to the cheaper class. Hence the system encourages science classes, but certainly does not encourage good science teaching.

Then, again, we have day schools, often calling themselves technical schools, which, on examination, will be found to be based entirely on the Science and Art Department syllabuses, and where lads who ought to be finishing their general education are being crammed up in all branches of science to pass the examinations and earn grants.

Surely the time has come for a change; there is great need for government help for technical and scientific education, but it should be given in a rational way. The starting of evening classes by individual teachers or in schools should be prohibited in all districts where organised technical schools exist. The organised schools should be helped not by payment on results but by a grant, according to the work being done. Let the department appoint representatives on the governing bodies of the colleges in proportion to the amount of money paid; let inspection be as rigorous as possible to see that sound instruction is given; but let it be by practical men of science, not by military officers, often ignorant of science; and do away with the May examinations altogether; then we might have a system of science teaching of which the country might be proud, and which would give really good results.

As a teacher of many years' experience, both of day and evening classes, I am convinced that the examinations do no good, but a vast amount of harm to teacher, student, and institution. Much good work has been done in classes in connection with the department, but it has been in spite of, not on account of, the examination system. Teachers look upon the examinations as unmitigated evils, but have to put up with them because the grant must be earned.—I am, &c.,

A. Humboldt Sexton.

Glasgow and West of Scotland Technical College, Glasgow.

THE NEW METHYLATED SPIRIT.

Sir,—There already exists one way, and so far as I know only one, whereby users of methylated spirit may still obtain it unadulterated with paraffin. Apply to the supervisor of the district for permission to purchase the spirit in quantity, direct from the manufacturers. The applicant will be required to specify the objects for which he proposes to use the spirit, and his statement and application will go to head-quarters. After the usual business of red tape and circumlocution, it will probably be allowed, and the applicant will then be required to find one surety in a bond for £200 as a safeguard against the application of the spirit to any improper uses. For this bond five shillings is charged. After these formalities are complied with, the holder of the permission is supplied with forms of requisition, and can order direct from the distillers. He also becomes a "user" of the spirit within the meaning of the recent order, and is entitled to requisition supplies free from paraffin. This is my own case, so that I can vouch for the correctness of my statements.

The method of procedure is roundabout and cumbersome, but it is apparently the only one whereby exemption can be obtained from the insane regulation which threatens to entail such disastrous consequences on British Science and Commerce. It is a marvel to me how the chemists of the Revenue Department could ever have excogitated and recommended an adulteration which, as they must have been aware, would have the effect of rendering methylated spirit practically useless in the laboratory. The matter should not be allowed to rest until this regulation is rescinded. Our laws are, indeed, fearfully and wonderfully made; and it is hardly strange that British science should show signs of languishing under its many discouragements.—I am, &c.,

Bryan Charles Waller, M.D., F.I.C.

Masongill House, Cowan Bridge, Kirkby Lonsdale, Jan. 11, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiii., No. 26, December 28, 1891.

Researches on the Application of the Measurement of Rotatory Power to the Determination of Combinations formed by Aqueous Solutions of Sorbite with the Acid Sodium and Ammonium Molybdates.—D. Gernez.—The author has previously shown that mannite, in contact with certain acid molybdates, undergoes an action which is revealed by a considerable change in the value of the rotatory power. The increase is so great that the reactions produced in the aqueous solutions of these bodies may be traced by the action upon polarised light. Sorbite, an isomer of mannite, admits of researches of the same nature.

Metallic Borates.—H. Le Chatelier.—The author considers that the only borates whose formulæ are established beyond dispute are the two hydrates of boric acid, BO_3HO and $BO_3,3HO$. The alleged compounds, $4BO_33MgO$, $3BO_32MgO$, and $2BO_3SrO$, are mixtures.

Isomeric States of Chromium Sesquisulphate.—The solid green sulphate, $Cr_2O_33SO_311H_2O$, although having the same composition as the violet sulphate, must have a constitution completely different. It does not behave like an ordinary salt, not admitting of double decomposition. It is probable that the chrome is involved in a radicle possessing a certain stability. On decomposing this salt with an alkali, there is precipitated, not the normal chromium hydrate, but a hydrate which takes up only 2 mols. of water.

Silicon Chlorosulphide.—A. Besson.—This compound, $Si_2Cl_2S_2$, is obtained by the limited action of chlorine upon silicon sulphide at bright redness.

New Crystalline Copper Phosphide.—M. Granger.—These crystals answer to the formula Cu_5P. If heated to redness in contact with air they are transformed into phosphate. They dissolve easily in hot nitric acid.

Solution of Antimony Chloride in Saturated Solutions of Sodium Chloride.—H. Causse.—Solutions of $SbCl_3$ precipitated by an alkaline carbonate may be rendered quite clear again by the addition of an excess of sodium chloride.

A Double Copper and Ammonium Cyanide.—E. Fleurent.—The double cyanide is stable; if dissolved in ammonia it takes a blue colour on exposure to the air; it is insoluble in cold water, and slightly soluble in boiling water, without change. Above 100° it loses ammonia, ammonium cyanide, which sublimes, and there remains cuprous cyanide.

Thermic Study of Bibasic Organic Acids: Influence of the Alcohol Function.—G. Massol.—The introduction of the alcohol function in an adjacent carbon deter-

mines a notable increase in the number of calories disengaged at the moment of the formation of the salts. In the succinic series, the number of calories disengaged increases with the number of alcoholic hydroxyls. In the same series, the increase bears entirely upon the first acidity; the addition of a second mol. of base liberates the same quantity of heat for all acids.

Disodium Glycol.—M. De Forcrand.—This paper is not adapted for useful abstraction.

Action of Dilute Nitric Acid upon Mononaphthene.—M. Konovaloff.—The principal product has the composition $C_9H_{17}NO_2$. With nitrous acid it gives a pale green colouration, due, perhaps, to the formation of a pseudonitrile.

Formation of Acetylene at the expense of Bromoform.—P. Cazeneuve.—Bromoform, in contact either with silver powder or with moist zinc-copper, is an abundant source of acetylene.

Action of Phosphorus Perchloride upon the Methylnaphthylacetones: Naphthylacetylenes, α and β.—J. A. Leron.—The author has prepared the two naphthyl acetylenes, which had not been previously isolated, and which he now describes. The α-compound is a liquid boiling at 296—298°. The β-compound is a solid, fusible at 51°5—52°.

Observations on a Paper by Arm. Gautier and R. Drouin.—Th. Schlœsing, jun., and Con. Laurent.—The authors consider that their results are somewhat obscured by the paper of MM. Gautier and Drouin. They have not announced, but demonstrated, the fixation of free nitrogen by inferior green plants.

Zeitschrift fur Analytische Chemie.
Vol. xxx., Part 4.

Heating Appliances for Laboratory Use.—A number of devices by G. Barthel (*Helfenberger Annalen*). G. Barthel's benzene-burner (same source); Swoboda's petroleum lamp (*Pharm. Zeit.*); Bevington H. Gibbins's oil-gas lamp (CHEMICAL NEWS); paraffin-gas in laboratories by F. W. Boam (CHEMICAL NEWS); gasoline muffle-furnace by E. R. Ellis (*Jour. Soc. Chem. Ind.*); improved spirit lamp, M. T. Lecco (*Chemiker Zeitung*); combination of three gas-burners, F. W. Branson (*Jour. Soc. Chem. Ind.*); improved Bunsen-burner, L. Reimann (*Zeit. Angewandte Chemie*); further improvements by J. R. Griffin (*Jour. (Soc. Chem. Ind.)*; universal burner, A. Stutzer (*Zeit. Angewandte Chemie*); improved gas-lamp, Max Gröger (*Zeit. Angewandte Chemie*); burner for heating water-baths; the Dessaue gas-works (*Zeit. Angew. Chemie*); heating-worms, F. Lüdtke (*Chemiker Zeitung*); evaporation apparatus, F. E. Ray (*Jour. Soc. Chem. Ind.*).

Potash Apparatus for Ultimate Organic Analysis.—A. Delisle (*Dingler's Journal*).—This apparatus cannot be described without the accompanying figure.

Apparatus for Extraction.—A number of appliances are here briefly described, for accounts of which we must refer to the original.

Distillation of Mercury in a Vacuum.—W. Dunstan and T. S. Dymond.—(From the *Philosophical Magazine*).

Renovation of Caoutchouc Articles.—(*Central Zeitung fur Optik*).—The articles are steeped in a mixture of two parts water and one part ammonia. In a few minutes, or at most in half an hour, they recover their elasticity.

Inferior Filter Papers.—L. Padé.—In an average sample of ordinary white filter paper the author found 10·4 per cent of ash.

Table of Specific Gravities of Aqueous Nitric Acid.—G. B. Squires.—(From the *Pharm. Era*).

Preservation of Aqueous Sulphuretted Hydrogen.—A. J. Shilton.—(From the CHEMICAL NEWS.)

Influence of Nitrous Acid upon the Specific Gravity of Nitric Acid.—R. Hirsch (*Chemiker Zeitung*).—Each per cent of nitrous acid raises the specific gravity of the nitric acid by 0·01.

Recovery of Silver Residues.—H. Hussenot.—If such residues are in solution they are mixed with ammonia in excess, and from this ammoniacal solution the silver is precipitated by the immersion of a piece of copper. If the residues are insoluble in water and ammonia, they are first boiled with sulphuric acid. Chlorine, bromine, &c., are expelled, and copper sulphate is formed, which is rendered alkaline, and the silver is precipitated with copper. The silver thus obtained may be used for the production of silver nitrate. The ammonia and sulphuric acid need not be pure.

The Use of Oxycellulose for Analytical Purposes.—The power of oxycellulose to attract and fix colouring matters and in general bases (even from saline solutions), induced MM. Witz and Osmond to ascertain whether this attraction might not be applied for the detection and determination of small quantities of the substances precipitated in this manner. The authors have first occupied themselves with the determination of vanadium, and have found that it can be precipitated in this manner. In order to conclude as to the quantity of vanadium, they use it for the production of aniline black, and compare the intensities of the shades produced under corresponding conditions.

The Preparation of Pure Phosphoric Acid.—A. Joly.—(From the *Bulletin de la Societé Chemique*).

Oxidation of Sulphides by the Action of the Electric Current.—E. Hintz.—An illustrated memoir from the *Journal of the Franklin Institute.*

Separation of Iron from Cobalt, Nickel, and Manganese.—Alonzo C. Campbell.—(From the *Journal of Analytical Chemistry*).

Determination of Arsenic in Iron.—F. W. Boam.—(From the CHEMICAL NEWS).

A Novel Fatty Acid.—A. Gérard.—(From the *Comptes Rendus*).

Qualitative Recognition of Glycerin.—C. A. Kohn.—(From the *Journal of the Society of Chemical Industry*).

A Sensitive Reaction for Tartaric Acid.—Ed. Mohler.—Already noticed.

Determination of Nitrogen.—A number of improvements in the known processes by Berthelot (*Soc. Chim.*); Buchan (CHEMICAL NEWS); Aubin and Quenol (*Soc. Chimique*); J. A. Müller (*Annales de Chimie*); improvement in the Kjeldahl process, R. Meldola and E. R. Moritz (*Journ. Soc. Chem. Ind.*); comparison of the methods of Dumas, Wanklyn, and Kjeldahl, by Oddy and Cohen (*Journ. Soc. Chem. Ind.*).

Basicity of Organic Acids.—D. Berthelot.—(From the *Comptes Rendus*).

Determination of Acetic Acid in Acetone, Vinegar, &c.—J. A. Wilson.—(*Journ. Soc. Chem. Ind.*)

Determination of Aniline and Monomethylaniline.—F. Reverdin and Ch. de la Harpe.—Already noticed.

Determination of Free and Combined Acid in Hydrochloric Solutions of Hydroxylamine.—J. A. Müller.—According to the author, there is required only a simple titration with alkaline carbonate, using phenolphthalein as an indicator. Free hydroxylamine has no action upon phenolphthalein. The same holds good with the amines.

Determination of Sugars with Solution of Copper-Potassium Carbonate.—H. Ost.—(*Berichte Chem. Gesellschaft*).—The author has already discussed the determination of inverted sugar, of dextrose, levulose, galactose, arabinose, and lactose, and now takes up maltose. This sugar reduces much less cuprous oxide

than do the monosaccharides, and about half as much as inverted sugar.

Determination of Methoxyl and its Special Applications.—Extracts from the *Chemikr Zeitung* and *Monatshefte für Chemie.*

Determination of Lignine in Woods.—R. Benedikt and M. Bamberger (*Monatshefte fur Chemie*).—Already inserted.

Examination of Chinese Tea.—P. Dvorkovitsch (*Berichte Deuts. Chem. Gesell.*).—This memoir will be inserted *in extenso.*

Contributions to the Chemical and Microscopic Examination of Coffee and its Adulterants.—C. Cornauth (*Mittheilungen aus dem Pharm. Institut der Universität Erlangen*).—No particulars are given.

Rapid Volumetric Determination of Metallic Zinc in Zinc-Powder.—F. Weil (*Bull. de la Soc. Chimique*).—Already inserted.

Examination of Commercial Picric Acid.—A. H. Allen.—(From the *Jour. Soc. Dyers and Colourists*).

General Process for Examining Fatty Lubricants.—L. Archbutt.—(From the *Jour. Soc. Chem. Ind.*).

Determination of Mercury in Poisoning Cases.—Ludwig (*Zeit. Apotheker Vereins*).—Already inserted.

The Atomic Weight of Cadmium.—E. A. Partridge.—(From the Chemical News).

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xv., No. 3.
This issue contains no chemical matter.

MISCELLANEOUS.

Detection of Paraphenetidine in Phenacetine.—L. Reuter.—The author finds the reaction of the poisonous paraphenetidine with solution of iodine as less sensitive than that with chloral hydrate.—*Zeitschr. Anal. Chemie*, xxx., Part 4.

Action of Isoamyl Iodide upon Trimethylamine in Aqueous Solution, in the cold in Equimolecular Proportions. Trimethylisoamylammonium.—H. and A. Malbot.—We might expect that isoamyl iodide would yield a quaternary ammonium with trimethylamine; but the activity of tri-isobutylamine is less than that of tri-isoamylamine for one and the same ether. Hence we cannot obtain a tetrabutylammonium iodide.—*Bull. de la Soc. Chim. de Paris*, vi., No. 10.

The New Methylated Spirit.—An eminent medical organ learns that in future half per cent of *wood naphtha* (*sic !*) is to be added to methylated spirit. Our contemporary imagines that the mixture will be "absolutely undrinkable,"—which is a mistake. He is aware that the new concoction will be unwelcome to photographers and others, but he thinks that in such a case their complaints should be disregarded. We hold, on the contrary, that an injury to research and to the organic chemical manufactures will be poorly compensated by a hindrance thrown in the way of a few desperate drunkards. It is not too much to say that the Act permitting the sale of methylated spirits is completely stultified by this most mischievous innovation.

Patent Law.—The *Chemiker Zeitung* makes mention of a decision given by the German Patent Office and confirmed on appeal by the Supreme Courts. A foreigner held a German patent for a machine for mincing meat. The patentee made large machines for butchers, &c., in Germany, but the small machines for household use he made abroad and exported them to Germany. This was held to be a contravention of Section 11 of the Patent Law, and the patent has been cancelled. In Britain every alien may hold a British patent without any intention to carry it out wholly or partially in this country. Thus our patent system is made to keep trade out of the country instead of promoting its introduction.

On the Nature of so-called Actions of Contact.—E. Ritsert (*Chem. Centralblatt*). — So-called contact actions, as occasioned under certain circumstances by platinum sponge, wood-charcoal, glass-powder, &c., may be explained by the assumption that the mols. of the active body in question by their vibration modify the vibrations of the bodies submitted to contact, and thus effect their combination. Thus, *e.g.*, the mols. of hydrogen and oxygen on contact with the mols. of platinum undergo such a modification of their vibrations that they take place simultaneously, but in opposite directions; whereby, according to the hypothesis of Bjerkness, a chemical union may be effected. The effects of the ferments may be explained in an analogous manner.

MEETINGS FOR THE WEEK.

Monday, 18th.—Medical, 8.30.
Tuesday, 19th. — Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
Wednesday, 20th.— Society of Arts, 8.
—— Meteorological, 7. (Anniversary).
—— Microscopical, 8. (Anniversary).
—— Geological, 8.
Thursday, 21st.—Royal, 4.30.
Royal Society Club, 6.30.
Chemical, 8. "The Estimation of Oxygen in Water, by M. A. Adams. "A Pure Fermentation of Manitol and Dulcitol," by P. F. Frankland and W. Frew. "The Luminosity of Coal-gas Flames," by V. B. Lewes. "The Magnetic Rotation of Dissolved Salts," by W. Ostwald. "On the Dissociation of Liquid Nitrogen Peroxide, by W. Ostwald.
—— Royal Institution, 3. "Some Aspects of Greek Sculpture in Relief," by A. S. Murray.
Friday, 22nd.—Royal Institution, 9. "The Composition of Water," by The Right Hon. Lord Rayleigh, F.R.S.
—— Physical, 5. "On the Driving of Electromagnetic Vibrations by Electromagnetic and Electrostatic Engines," by Prof. G. F. FitzGerald, F.R.S. "On Supplementary Colours," by Prof. S. P. Thompson, F.R.S.
Saturday, 23rd.—Royal Institution, 3. "The Induction Coil and Alternate Current Transformer," by Professor J. A. Fleming, M.A., D.Sc.

Erratum.—P. 13, column 1, line 9 from bottom, *for* "leader" *read* "reader."

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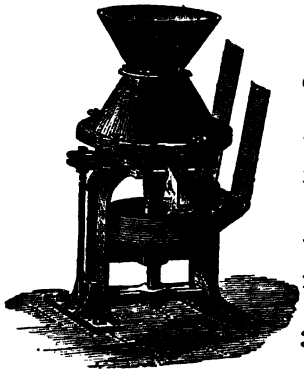

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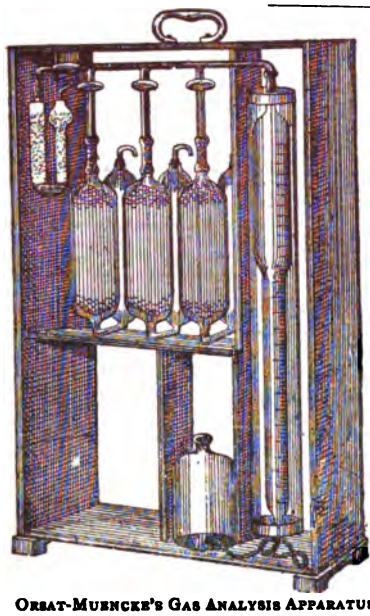

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THE CHEMICAL NEWS.

VOL. LXV., No. 1677.

ON THE

IODINE NUMBER FOR LARD OIL BY THE HÜBL METHOD.*

By REUBEN HAINES.

SEVERAL years ago the writer made a large number of examinations of various oils and fats by the Hübl method, including among them lard oil. Although several determinations of the "iodine number" for lard oil have been published, the writer thinks it worth while to put upon record the results which he had obtained.

Three samples of lard were first obtained, two of them directly from two lard factories put up ready for the market, and expressly stated to be pure articles; and the third sample from a farmer who was accustomed to serve the writer's family with lard. These lards were tested for purity by tests in use at that time, and all were passed as genuine and unadulterated. The two factory lards had a melting-point of 45° C., while the country lard was much softer and had a much lower melting-point (33° C. was found, but this was possibly 2° or 3° too low). The iodine numbers found for these samples of lard were as follows:—

Factory lard No. 1 (average of	3	tests)		62·30
„ „ No. 2	4	„		62·49
Country lard	2	„		59·33

The oil was then pressed out of each sample separately in the laboratory by means of an ordinary hand drug press, the temperature of the room being regulated to an average slightly below 50° F., never exceeding 55° nor going below 45°, the time of year being favourable for that object.

The pressure of the screw was gradually increased to the utmost that the press was capable of producing.

The oils obtained from these lards did not chill or become turbid until about 45° F. The temperature maintained in the pressing and the "cold test" of the oil produced are identical with factory practice. On being submitted to the Hübl test these oils gave the following results for the iodine number:—

Oil from Factory lard No. 1 (average of	5	tests) ..		75·14
„ „ „ No. 2		„ „ ..		73·03
„ Country lard		„ „ ..		70·01
Average for oil from both factory lards				74·01
„ „ the three oils..				72·72

These oils contained free fatty acid equivalent to oleic acid 0·86 per cent, 0·49 per cent, and 1·35 per cent, respectively, a short time after the above iodine numbers were obtained.

A peculiarity noticeable which I am unable to explain is the fact that the country lard of low melting-point, and also the lard oil made from it, have lower iodine numbers than the other lards and the oils from them. Nevertheless, the tests were all made with equal care to avoid error.

The same two oils made from factory lards were recently tested by the modified Bechi test (omitting the rapeseed oil and amyl alcohol, and acidifying only very slightly with nitric acid), but no darkening of colour was produced after heating exactly fifteen minutes on a water bath. The sample of oil from country lard was lost, and was not tested in this manner. There had been but slight increase in acidity in the oils from factory lards.

A sample of prime lard oil was obtained from a reputable dealer, who guaranteed it to be strictly pure from their knowledge of the manufacturers of it. This oil was obtained at about the same time as the above mentioned samples of lard. On being tested by the Hübl method the iodine number was found to be 74·02 as the average of four consecutive tests. It was also examined recently by the above modified Bechi test, and it did not become darkened in colour. The rise of temperature by Maumené's test was found to be 42° C., the experiment being made in the manner recommended by Allen.

Recently, also, the iodine numbers for the oil made from factory lard No. 1 (same sample as tested before), and for the above mentioned sample of prime lard oil were re-determined with very great care in regard to the details of manipulation. The following results were obtained:—

Oil from Factory lard No. 1 (two consecutive tests)	72·34; 72·33
Prime lard oil (single test)	73·73

The difference from the former figures may have been largely owing to the fact that in these later tests greater care was taken to secure perfect uniformity of temperature during the experiments, and to have a large excess of iodine in the titration, about equal to the quantity absorbed by the oil. In the former experiments the titrations were made at the expiration of two to three hours; in the latter ones the time was extended to six hours. Three hours is, however, found to be sufficient for non-drying oils. In the last experiments a burette with a glass stopper at the top and a small hole for admission of air was used for the iodine solution instead of closing an ordinary burette with a cork as was done previously. A delicate thermometer was kept constantly almost in contact with the burette. Equal measured quantities of potassium iodide solution and of chloroform in the tests and blank experiments, and only the purest chloroform was used; in the last experiments chloroform of the grade used for inhalation in medical practice.

* *Journal of Analytical and Applied Chemistry*, Vol. v., No. 5.

UPON CERTAIN CONSTITUENTS OF THE "NITROGEN FREE EXTRACT."

By W. E. STONE,
Purdue University, La Fayette, Indiana.

SOME study of the constituents of feeding-stuffs, reported elsewhere in detail (*Amer. Chem. Journ.*, xiii., 73; *Ber. d. Chem. Ges.*, xxiii., 3791), point to the presence in such materials of a distinct class of bodies which, so far as our analytical methods go, may and do pass unrecognised under the comprehensive head of nitrogen-free extract matter. These are the gum-like carbohydrates which upon hydrolysis yield the pentaglucoses or pentoses, *arabinose* or *xylose*, as the case may be. By means of the furfurol reaction, which is peculiar to these bodies and their derivatives, I have shown that many of our feeding-stuffs contain very appreciable quantities of the same, particularly those of fibrous or woody nature like hay, straw, bran, maize, brewers' grains, &c.

These bodies are practically insoluble in water and alcohol, but are extracted from tissues by heating with weak alkalies, and in the same way are converted into sugars (the pentoses) by treatment with dilute acids. In the course of an ordinary fodder analysis these bodies would therefore succumb to the operations directed against the carbohydrates, and would increase their apparent proportions in the material, whether determined indirectly as nitrogen-free extract or directly by their reducing effect after inversion. Agricultural chemists have recognised the desirability of some more definite knowledge of the usually large amount and widely differing

bodies referred to broadly as nitrogren-free extract, and the same is equally true of the great variety of nitrogenous bodies which find no intelligent expression in the "crude protein" of analytical results. My studies of the pentoses and the bodies from which they are derived have been made with the desire to throw some light upon the first-named class.

While recognising the varying character of the nitrogen-free extract, the most satisfactory disposition heretofore made of it has been to oonsider it as a whole, of carbohydrate nature, and upon this basis has been developed the current views with regard to the digestibility of foods, digestion coefficients, nutritive ratios, and general valuation based on composition.

Doubtless very grave errors are comprehended in this system because of the non-recognition of the variable nature of those non-nitrogenous bodies which succumb to the action of dilute boiling alkalies and acids. In other words, the reactions upon which are based the specifications of the carbohydrates are far too general to serve as a basis for what is ostensibly so important a matter as a digestion experiment. The following examples will show the fallacy of this sweeping classification:—

Maize meal contains about 80 per cent of nitrogen-free extract, which is largely farinaceous, and as such is easily subject to digestion or other destructive action. Wheat bran which contains proportionally very little starch shows nevertheless about 65 per cent of nitrogen-free extract, which we are not justified in valuing like that of the maize, nor may we assume an equal degree of digestibility. Brewers' grains which have undergone a process of malting and brewing expressly intended to remove all bodies of the nature of starch and sugar, yield after all upwards of 50 per cent of nitrogen-free extract. If the bran or brewers' grains be subjected to the action of dilute acids, however, the resulting products will reduce Fehling's solution as if a true sugar were present. Approaching this fact from another direction we find that both bran and brewers' grains contain large amounts of those materials which upon inversion yield the pentoses.

Having recognised the existence of these different classes of non-nitrogenous bodies, have we any authority for ascribing to them equal digestibility or nutritive value? The data bearing upon the subject are very meagre. Prof. Kühn designates the mucilages and gums to which these bodies belong as of doubtful nutritive value ("Ernährung des Rindviehs," Ninth Edition, p. 60). Gorup-Besanez regards gums, mucilages, and pectin substances as not digestible in the strict sense ("Physiologische Chemie," Second Edition, p. 767). Indirectly the experience of Gudkow (*Zeitsch. fur Chemie*, 1870, 360) throws considerable light upon the matter. Recognising in wheat-bran the existence of a peculiar body which resembled the true carbohydrates in yielding a reducing sugar, he endeavoured to isolate it from the true carbohydrates, and especially starch, by malting. Failing in this he caused bran to be fed to swine, and found that while starch and other carbohydrates were digested, the particular object of his study was not, that it passed through the digestive tract undestroyed; and from the dung of the animal he succeeded in preparing the inversion product, which resembled the ordinary glucoses, but was not identified. This indigestible portion of the nitrogen-free extract of bran was afterwards identified in part by Prof. Tollens and myself (*Liebig's Annalen der Chemie*, 239, 249), and wholly so by Steiger and Schulze (*Ber. d. Chem. Ges.*, xxiii., 3110), as one of the pentose-producing gums.

No digestion experiments bearing upon these bodies have been made, because, until within a short time, no methods for their recognition or determination have been available.

I have, however, tested the dung of animals for substances of this class with positive results. The manure of steers fed upon a diet composed largely of maize ensilage yielded an amount of furfurol equivalent to 5 per cent or more of these bodies. Manure from the same animals a period when their diet was composed largely of dry maize fodder, yielded the equivalent of 7 per cent or more of these substances. It is, moreover, highly probable that these percentages are much too low, owing to the incomplete methods by which they were obtained. They serve to show, however, that these bodies resist digestive action to a good degree.

In the light of this it is impossible to resist the belief that the indigestible carbohydrates recorded as such in digestion experiments are to a large extent of this class, and that digestive action is more selective in its action than our analytical methods. That is, while we assume an equal value for a large group of materials, they do not show the same behaviour toward digestion, so that the undigested carbohydrates found in the dung of an animal may represent in the main only a particular class of the whole, and possess quite different nature and value from those which have been digested. As to the absolute digestibility of these bodies I hope to gain some light by direct digestion experiments, which methods now at hand render possible.

Also in this same connection, viz., the ability of these substances to resist destructive forces, it is of interest to note this occurrence in ensilage. Both maize and clover ensilage which was well preserved, but had undergone the usual fermentative changes largely destructive to the true carbohydrates, such as starch and sugar, were examined and found to contain appreciable quantities of the pentose gums.

We are therefore able to differentiate from the true carbohydrates in the nitrogen-free extract a group of bodies which are undoubtedly of less nutritive value than the former, and which are resistant toward digestive and fermentative action to an appreciable extent.—*Agricultural Science*, vol. v., No. 4, April, 1891.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Concluded from p. 28).

No notion has perhaps interfered more with the natural development of physiological chemistry, and consequently with the insight into the cause of the chemical difference of organisms and their germs and ova, than the tacit assumption that it is possible to apply at once the principles which hold good in the ordinary reactions of organic and inorganic chemistry to the chemical processes in the living cell, which take place in the smallest spaces generally at much lower temperatures and at higher tensions. Pflüger alone (as early as 1875) has in part set himself free from this prejudice and has recognised the "self-decomposition" of the mols. in living protoplasm.

The view, however, still appears universally prevalent that the chemical difference of living beings depends on the difference of chemical compounds and on their dissimilar arrangement in the tissues. But that such cannot be the case has been already shown in a universally valid manner, even without the deduction laid down in this memoir.

If, for instance, the difference of a mammal and a bird from a chemical point of view depended on the difference of the compounds capable of production from their bodies or their arrangement, then the difference of two mammalian species, sub-species, or sports, or even of two individuals of the same kind, must depend on the same causes. There must, *e.g.*, be contained in the egg from which a cock is evolved different chemical compounds from one which yields a hen, and every pair of eggs from which a couple of hens issue must contain dissimilar chemical compounds, since no two chicks just escaped from the shell are identical. If we are willing to adhere to this conclusion we should refute the entire principle which has been set up, for a chemical compound is in the

spirit of chemistry always—theoretically at least—capable of being produced, and must therefore occur more than only once, otherwise it would be no chemical compound. Living individuals, no two of which are so closely identical as two lots of one and the same chemical compound, must therefore, since they exist only once, be distinguished from each other by something beyond dissimilar chemical composition.

This something beyond cannot be found in a different arrangement of perhaps identical chemical compounds, since the arrangement of the chemical compounds in every individual being changes continually, otherwise it would cease to live.

Nothing therefore remains but the inference that in every living being the manner in which the chemical processes take place in it—that is to say in its protoplasm—is unlike. It is unlike because the protoplasm is of all natural products by far the most impressionable, *i.e.*, the most dependent upon imperceptible outer influences, and on account of its smallness, which excludes the action of mass at the decisive place (in the capillaries), it is unable to react on one occasion exactly the same as on another. So long as it has not accommodated itself to exactly the same external conditions (which can never be effected) it must behave differently. Hence, however strongly heredity may tend to the production of stable states under conditions which differ relatively little, it is impossible that two identical individuals should ever be produced. They would have to originate without protoplasm, like two crystals of felspar, of which we may at least suppose that they are distinguished by nothing other than their duality.

But we need no proof that no living being arises without protoplasm, and that no twin is so similar to its cotwin as one crystal is to another. Hence, as we have long been convinced of the accuracy of these general considerations, we have directed our attention much less to them than to the especial consequences of the view here presented on the nature of the chemism in living protoplasm and its dependence on the nature of the organic elements, and we hope shortly to demonstrate experimentally that an artificial imitation of the morphological relations, which are realised in the protoplasm of the plant cell and of the animal cell, yields principally the same results as the organism, at least as far as certain biochemical processes are concerned.

Of a "vital force" there can then remain, from a chemical point of view, nothing at all.

ON THE

DETERMINATION OF THE MELTING POINTS OF MINERALS.*

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., D.Sc., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

(Concluded from p. 32).

The Eye-Piece Galvanometer.

To render it more convenient to observe the deflection of the galvanometer simultaneously with the melting of the substance, or whatever other phenomenon we are observing upon the ribbon, I use the following arrangement:—A small galvanometer coil, wound with fine wire and containing a freely pivoted magnetised needle, is affixed to the eye-piece of the microscope. Projecting from the needle at right angles to its length, and entering a horizontal slot in the eye-piece, is a fine index-hand. This moves across the margin of the field, being accurately in the plane of the image formed within the eye-piece by the lower optical train. Its motion is confined to a small arc, the magnetised needle without being stopped by pins at either side. This renders it fairly dead beat. When no current is passing the needle points to the centre of the field under the influence of a small control magnet affixed to the coil. Binding screws enable this galvanometer to be circuited with the larger galvanometer, which stands upon the table, and the Leclanché battery. This is a *very* great addition to our power of effecting an accurate measurement.

Appearances of Melting.

The appearances which characterise melting vary according to the nature and properties of the substance. A viscous substance is seen to round its angles slowly, the smallest fragments going first. If the temperature is well over the softening point the process is rapid, and spreads from small to large fragments, the whole coalescing finally in pools upon the platinum. It is always possible in such cases to fix a temperature at which the substance decisively melts, and one at which prolonged heating seems hardly to effect it. But, as already observed, softening may occur at temperatures much below the earliest visible phenomena of melting.

In the case of substances which melt rapidly and recrystallise on solidification, it is easy to fix the melting-point very closely. In fact, the temperature may be so regulated that the small passing changes of temperature affecting the ribbon determine fusion or solidification; the result being that the salt appears as if vibrating between the solid and the liquid states, rays of crystallisation darting across its surface, or again melting at the edges. These bodies are very easily dealt with; the salts selected for calibrating the ribbon, *i.e.*, for the construction of the curve, are of this nature, as the carbonate and nitrate of potash, as well as potassium bromide. Silver chloride is also a salt of this nature, but it possesses also the peculiarity of changing colour when melting. Solid, it is a greenish-white, crystalline substance; melted, it is an amber-coloured liquid, deepening in colour with rise of temperature. The passage from the one state to the other is a well marked point. Similar phenomena mark the melting-point of silver sulphate. If the substance is a metal the melting-point is looked for in either of two ways. We may scrape a little dust off the metal on to the platinum ribbon, and, raising the temperature continually, catch the reading when the little fragments suddenly run down. A second trial, in which we may more carefully approach the melting-point, will fix a correct reading. In the cases of silver and palladium, we may observe the behaviour of a pool of the previously melted metal; when such is again just melting a change of colour of the surface is visible. The appearance is as if a red or yellow flush (according to the temperature) passed across the surface; it is very characteristic, and seems due to the smoothing of the rugosities on the solid substances which keep the surface darker by their greater area of radiation. Points determined in this way, in the case of silver and palladium, agree with the points determined by observation of the breakdown of very small scrapings of the metal. It is to be observed that metals should be determined only on the first or second melting, as there is risk of mutual solution or alloying with the platinum, which would affect the melting-point. In general, it may be said that the breakdown of very small fragments, or a rocking motion apparent in the larger fragments, are the readiest, and probably the surest, signs of melting.

Range of the Meldometer and its Degree of Reliability.

Coming now to the consideration of the range possessed by this apparatus for the comparison of melting-points—for such it obviously is—it will be convenient to refer to the curve of melting-points obtained by observations on the meldometer, such as I have described. The points fixed on the lower part of the curve are based, principally in the results of Carnelley (see his "Melting-

* A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

and Boiling-Point Tables"), or the *résumé* of his results given in the *Physikalisch-chemische Tabellen* of Landholt and Bornstein. Carnelley and Williams's observations were made by a calorimetric method, in which they heated a platinum vessel to the temperature at which the salt melts, and plunging the platinum in water determined the quantity of heat contained in the platinum at the unknown temperature (Carnelley and Williams, *Journ. Chem. Soc.*, vol. i. (1876), p. 489). The specific heat of platinum had been measured by Pouillet, by direct comparison with the air-thermometer up to 1200° C. (Pouillet, *Comptes Rendus*, vol. iii. (1876), p. 782). The data so obtained are used by Carnelley. This physicist was so well acquainted with the whole subject that it appears hardly possible to say more in their support than that he was satisfied to accept them as the best basis available whereon to investigate and discuss the periodicity of the melting-points of certain groups of compounds.

Violle (*Comptes Rendus*, vol. lxxxv. (1877); vol. lxxxvii. (1878); vol. lxxxix. (1879), finding the variation of specific heat with temperature by reference to the porcelain air-thermometer, determined the melting-points of silver, gold, copper, palladium, &c. His determinations, therefore, rest on a similar basis to those of Carnelley.

The whole question has been recently reviewed very completely by Herr Carl Barus, for the U. S. Geological Survey. (*Bulletin* No. 54, 1889).

Assuming the reliability of Pouillet's investigations, there appears little doubt that, so far as Carnelley's observations extend (900° C., about), they are probably the most reliable yet made; although it is probable—almost certain, indeed—that there is a *small* minus error increasing with the temperature of melting (see account of his method *loc. cit.*). It is, perhaps, a further proof of their reliability that their agreement *inter se* appears very close. If we assume the co-efficient of expansion of platinum to preserve a fairly uniform value over this range we find, from observations on the meldometer, that his data closely lie along a common line. The agreement is still closer if we assume a slow, fairly uniform rate of increase of the co-efficient of expansion (*à priori* probable); and this assumption enables us, also, to extend the line, through the careful results of Violle, for the highest temperatures. Thus, silver 954° C., gold 1045° C., and palladium 1500° C. fall upon such a slow curve as is seen in the plate. Violle's results, which, as observed, are also calorimetric, and are admittedly of much value, are, in fact, singled out by Carnelley in his "Melting- and Boiling-Point Tables," as specially reliable. By using these points of Violle's we may extend our knowledge of the melting-points of minerals up to (and safely somewhat beyond) the temperature of 1500° C. with the same degree of accuracy attained in the research of Violle. Pure palladium is supplied by Messrs. Johnson and Matthey. Pure precipitated gold (1045° C.) should be used if this substance is experimented on. It is to be spread in fine dust upon the ribbon, and the moment at which the particles break down seized as the melting-point. I have found by interpolation upon the curve that precipitated black oxide of copper, CuO, melts at nearly the same temperature (at 1055° C.), and as this substance breaks down at once, I suggest it as a substitute, giving a convenient point upon the curve between silver and palladium. Its *first* breakdown must be observed, as upon re-melting phenomena occur which render the melting-point difficult to distinguish. Copper (1054° C.) is difficult to deal with owing to oxidation; on the meldometer it is hard to distinguish its melting-point from that of gold.

At the very highest temperatures the platinum ribbon reveals a certain amount of viscous stretching. It was very important to determine the amount of this, and its influence in setting a limit to the range of measurements. Observations were accordingly made in which the temperature was raised by different amounts, and the behaviour of the ribbon observed over intervals of five minutes. Where viscous extension took place the ribbon, of course, did not return to its initial length. The true expansion in such cases was deduced by deducting from the whole extension the observed amount by which it failed to return to the initial length. From the extensions the temperature was computed as described, and the following table obtained:—

Temperature, ° C.	Duration of Heating.	Viscous Extension.
1430	5 minutes	0·0
1510	5 „	0·0002
1565	2 „	0·0004
1620	5 „	0·0010
1780 (?)	3 „ (stretching rapidly)	0·0033

Length of ribbon closely 3·80 inches.

A viscous extension of 0·0001 introduces an error of about 3° C. It was observed, too, that at the temperature of melting palladium (1500°) a small viscous extension was sometimes apparent, and also upon prolonged exposure to the temperature of melting quartz. But it is evident that the error introduced by this effect, even if neglected, would not at a temperature so high as 1500° C. maintained for five minutes be a source of serious error. I think the allowance for it which can readily be made by reading the new length l_1, after the observation, may be considered to eliminate its effects. Thus producing the curve beyond Violle's result for the melting-point of platinum temperatures so high as 1600° C. are determinable, and for their accuracy may with considerable assurance be referred to the degree of accuracy attained by Violle in his determination of the melting-point of palladium. So high as 1700° the results obtained with this apparatus will still possess an approximation to this same degree of accuracy.

Drawing the Curve.

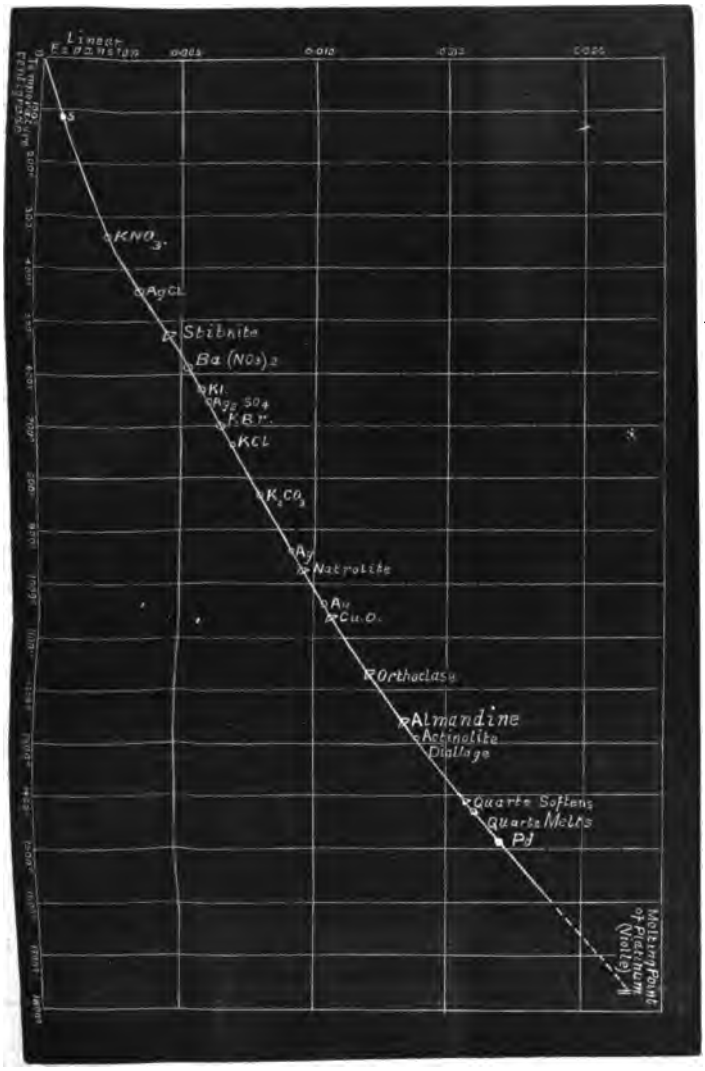
A single numerical example of the method of finding a point upon the curve may be of service. Thus, in the case of silver chloride, at starting we find the head of the screw reading 1098 divisions from the zero point, the temperature being 15° C.; when the salt is melting we find the head reads 1242 or the advance has been 144. Now each of these represents an advance of the 1-100000th of an inch, the thread being pitched 1-100", and the head carrying 100 divisions. We measure, when cold, the ribbon by a divider, and find it reads 3·80". In taking this measurement we are not particular to scale the exact whole length; for although the ribbon is cut away at the ends in the manner before described (to favour uniform heating), it is seen to remain dark where *quite* close up to the forceps. It therefore conduces to accuracy to read the length about 1·100th of an inch less than its full length. The correction is evidently a very immaterial one in any case from the comparative nature of the observations throughout. The fraction $l_2 - l_1/l_1$ has now the value 144/38000 = 0·00379, which is accordingly plotted; conveniently to the scale 0·0001 to the m.m. This length is set off perpendicularly from the horizontal scale of temperature at the point 436° C. The melting-point is indeed given by Carnelley as 451° C., but the interval of temperature corresponding to the observed expansion is this value less the initial temperature of 15° C. This is the most convenient course to pursue if we wish to carry the curve through 0° C., which should be done if we desire to preserve it for continued use. Fifteen degrees higher up on the curve we may write AgCl, as is done on the drawing. In this manner the curve is constructed. An unknown temperature is evidently determined from an observed expansion by calculating the value of $l_2 - l_1/l_1$ corresponding to this expansion, and finding from the curve what temperature corresponds to such an ordinate. To this must be added a number of degrees corresponding to the initial temperature.

For determining the curve of melting-points, I have found the following substances convenient:—

	Degs. C.
Potassium nitrate	339
Silver chloride	451
Silver sulphate	654
Potassium bromide	699
Silver	954
Gold	1045
Or cupric oxide (first fusion)	1055
Palladium	1500

For verification of a new ribbon it is sufficient to select silver chloride, gold (or cupric oxide), and palladium.

upon the curve of expansions in the same manner in which I propose that mineralogists should determine the melting-points of mineral bodies. It is seen that in the apparatus described the mechanical arrangements are such that there is no magnification of the expansion at the point at which the micrometer is applied. If it was desired to apply this form of platinum-thermometer to more minute measurements, as over a more limited range of temperature, it is of course easy to secure more delicate indications by lengthening the spring which prolongs the movable forceps, so that we exaggerate at the micrometer the extension of the ribbon, or by lengthening



The foregoing method enables us to determine in a few minutes the melting-point of a substance on the same basis of accuracy as that attained by the most careful observers. Only a very minute quantity of material is required, a condition often desirable in dealing with mineral bodies, and often again with bodies prepared by the chemist. Perhaps the peculiar function of the meldometer will be best understood from the consideration that from any three or four of his numerous and laborious determinations, Carnelley might, by the use of such an apparatus, have at once arrived at the melting-points of the many other substances he dealt with, by interpolation

the ribbon itself. Thus doubling the length of the spring with the present dimensions of the ribbon secures a reading closer than one degree centigrade. The applications of such an apparatus—necessitating only the most minute quantities of substances for the determination of their melting-points—might be many in chemical research. On the other hand, however, it must be observed that it appears scarcely applicable to the determination of boiling-points, at any rate of volatile liquids, my limited experience in this direction indicating that the small quantity of the liquid is soon evaporated, and the indications of boiling difficult to catch.

Explanation of Plate.

The points on the curve marked by circles are the melting-points of assumed reliability from which, with the readings of, the meldometer for the expansion of the platinum ribbon, the form of the curve is determined. The points marked by triangles are melting-points found by the use of the curve so constructed.

ON A

RAPID METHOD FOR THE ACCURATE RECOGNITION OF SULPHIDES, ARSENIDES, ANTIMONIDES, AND DOUBLE COMPOUNDS OF THESE BODIES WITH METALS.*

By CHARLES A. BURGHARDT, Ph.D., &c.

The process to be described has been applied to the minerals mentioned below, but I have no doubt that all similarly constituted minerals will also be easily recognised by the method.

I am quite sure that all mineralogists have experienced much annoyance and difficulty in obtaining really satisfactory results with the ordinary blowpipe reactions in regard to some of the compounds of arsenic, antimony, and sulphur with metals, particularly in the separation of the metal or metals from the above-mentioned elements. In order to obtain the metal, the assay requires a most careful and tedious roasting on charcoal in the *oxidising flame* of the blowpipe, in order to volatilise away the sulphur, arsenic, or antimony. When this roasting is complete the residue (oxide) is mixed with either sodium carbonate, or that salt and cyanide of potassium, and fused for a considerable time on charcoal in the reducing flame in order to obtain a bead of the metal. Sometimes borax is used to eliminate a metal from a mixed oxide residue, dissolving one oxide and leaving the other. If the oxides left after the oxidising process above-mentioned are not soluble in borax, then the bead which is obtained in the subsequent reducing process is an alloy, and practically useless as a means of recognition of the metals entering into its composition. Having often been disappointed with the results obtained by the above-mentioned blowpipe processes, I determined to find, if possible, a more rapid and certain method of analysis of minerals.

The apparatus required is that which all mineralogists have been in the habit of using for a long period, viz :—

1. Small porcelain crucibles.
2. Test tubes.
3. A small platinum basin and a platinum crucible.
4. A platinum spoon made rather deep, something like a platinum crucible with a handle.
5. Hard glass tubing, closed at one end and about 4 in. long; a cork is placed in the open end, with a hole bored through it, and a hard glass tube of small bore passed just through the cork. The straight piece outside the cork is bent either *twice* at right angles (if required to pass vapours into water or solution), or *once* at right angles and drawn out to a fine nozzle if required to test for arseniuretted or antimoniuretted hydrogen.
6. A Bunsen burner of the ordinary type, or a spirit lamp.
7. Funnels, beakers, porcelain evaporating basins, stir rods, &c., &c., and small pieces of clean sheet iron and sheet copper.

Reagents.

Ammonium nitrate	(solid)
Sodium nitrate	,,
Potassium bisulphate	,,
Metallic zinc	,,
Hydrochloric acid	(solution)
Potassium ferrocyanide	,,
Potassium ferricyanide	,,
Ammonia liquor	,,
Caustic soda	,,
Silver nitrate	,,
Stannous chloride	,,
Bichromate of potassium	,,

All the above reagents can be carried about in the dry solid condition for travelling, except the hydrochloric acid and the ammonia. With regard to the latter, it can be carried in the form of solid ammonium carbonate or ammonium sulphate; and the ammonia liberated from the respective salts in the usual manner, and passed either into the solution to be tested or else into water. I cannot at present give as easy a way of producing hydrochloric acid when it is wanted from dry materials, but think that it could be prepared in sufficient quantity by heating together in a glass tube (with delivery tube attached as described above) a mixture of potassium or sodium bisulphate and sodium chloride. Hydrochloric acid gas would then be liberated. Nitric acid is not required in this method at all.

Having thus briefly touched upon the present method of the treatment by the blowpipe of the minerals containing volatile elements, I will at once proceed to describe the method proposed by myself to attain the same object. The oxidising reagent I use is pure crystallised ammonium nitrate. This salt on being heated to about 250° C., decomposes, intumesces, and the products of its decomsition are nitrous oxide (N_2O) and water. *Thus the products are both gases, and nothing remains behind, which is certainly a very great consideration.* The nitrous oxide, at the high temperature used, rapidly gives up its oxygen to any element having an affinity for that gas, and oxidises it, so that finally the principal decomposition products of the original ammonium nitrate which are evolved as gases are nitrogen and vapour of water. The *modus operandi* is exceedingly simple. The mineral to be tested is crushed up and powdered into an exceedingly fine powder, a platinum or porcelain crucible is taken and filled to about one-fourth of its bulk with coarsely crushed ammonium nitrate crystals, then upon this about 0·5 grm. of the finely powdered mineral is placed, and the crucible and contents held with a pair of tongs over the Bunsen lamp, just in the flame. A violent reaction is at once set up, and care must be taken to withdraw the crucible from time to time from the lamp in order to avoid loss by boiling over the sides. Sometimes it is necessary to add some more ammonium nitrate crystals to the partially cooled "melt" in the crucible and heat again in order to complete the reaction. *An excess of ammonium nitrate cannot possibly do any harm, and it ensures success.*

The crucible having been allowed to cool, the contents are extracted with water and the solution separated from the insoluble matter. During the fusion of the mineral in the crucible, characteristic colours of various metallic salts are most distinctly observed; occasionally, therefore, the operator must watch this fusion closely. The fusion and lixiviation of the melt only occupy a minute or two when one has attained some experience, but the whole analysis need not exceed fifteen minutes even in complicated compounds. When melting the mineral in a glass tube with the ammonium nitrate, and passing the products of combustion into water, care must be taken to carefully dry the ammonium nitrate in a water oven previous to use, as it rapidly absorbs moisture from the air, and the water thus evolved in the fusion tube would cause the hot glass to crack. The thoroughly dried ammonium nitrate is conveniently kept in a well stoppered bottle.

Sulphides of Arsenic.

Orpiment (As_2S_3).
Realgar (AsS).

Fused in glass fusion tube with tube bent twice at right

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* From the *Mineralogical Magazine*, Vol. ix., No. 43.

angles, the open end of the delivery tube dipping into water. Sulphuric acid was found in the water in distinct quantity by the usual barium chloride test; therefore the mineral was a sulphide. In the fusion tube was a slightly coloured solid residue which could be eventually completely dissolved in boiling water; it gave the reaction for arsenic acid (with nitrate of silver) and all the other reactions for arsenic; mirror on being treated with metallic zinc and acid potassium sulphate, and the arseniuretted hydrogen, decomposed into metallic arsenic by heating the hard-glass delivery tube to redness. *The mineral was therefore arsenic sulphide.*

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

December 17th, 1891.

Dr. W. H. Perkin, F.R.S., in the Chair.

Messrs. William A. S. Calder, Arthur Colefax, Charles E. Eastick, Henry C. Jenkins, and Thomas Neilson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Adams, Broomfield Place, Smethwick; Francis B. Darbishire, 59, Elienstrasse, Dresden; James Hendrick, Laurel Cottage, Watermoor, Cirencester; Henry Hollingshurst, 2, Jentha Road, East Hill, Wandsworth; Frank William Lucas, M.A., 183, Belle Vue Road, Leeds; Ernest John Parry, B.Sc., Brooklands, Bensham Manor Road, Thornton Heath; William Pullinger, 27, Queen's Road, Oldham; Charles F. Seymour Rothwell, 82, Manson Street, Manchester; Thomas John Buckler Sandercock, Sidcup College, Sidcup, Kent; Henry John Spray, 15, Bucharest Road, Wandsworth; Alfred James Squires, 16, Lower Road, Newark, Notts.

Of the following papers, those marked * were read:—

75. "*The 'Gas-volumeter' and 'Gravivolumeter.'*" By G. Lunge (*cf. Proc. C. S.*, p. 168).

In the *Proc. C. S.* (No. 96, April 4, 1891), Professor Japp describes an instrument by means of which the observed volume of a single gas gives directly the weight of the gas. This instrument is based on the principle of reducing gases to a standard volume by means which are the same as those I first introduced in the "gas volumeter," but Professor Japp prefers to call it by another name "gravivolumeter." To this I objected in a brief note in the *Berichte* (xxiv., 1656), and Professor Japp has since replied in the last part of his full paper published in the *Transactions* of the Society (1891, lix., 894).

If it were merely a question of the name of an apparatus, I should not trouble the Society, as I have nothing to add to what I then said in the *Berichte*, leaving it to others to choose between the names in question. But in his answer to my objections Professor Japp has charged me with making contradictory statements and ignoring "a commonplace of physical measurement;" this compels me to ask the Society to publish my refutation of these charges.

In the *Berichte* (*loc. cit.*), I stated that the "gravivolumeter" is in point of fact absolutely identical with the "gas volumeter," but that by modifying the form of the regulator ("Reductionsrohr") which I prefer, Professor Japp has diminished the accuracy of the instrument. He remarks: "I fear I must leave Professor Lunge to reconcile these two statements." If he had referred to my original descriptions in the *Berichte* (dated February 14th, 1890) and the *Zeitschrift fur Angewandte Chemie* (March 1st, 1890), he would have had no difficulty in doing so.

My regulator contains a certain volume of air, which under "standard" conditions causes the mercury to rise to a fixed point, and by producing this condition simultaneously in the regulator and the gas burette, I reduce the gas contained in the latter to standard conditions also, thus avoiding in the measurement of the gas the necessity for observations of temperature and barometric pressure and all calculations connected therewith. My apparatus has completely realised this object, and Professor Japp has adopted the self-same principle and availed himself of the same means for effecting the reduction. It is manifestly indifferent, as far as the principle is concerned, whether the standard volume of air in the regulator is 25 c.c., or 50, or 100, as I have distinctly stated in a passage possibly overlooked by Professor Japp (*Ber.*, xxiii., 444, line 30). For the sake of obtaining more accurate results, I preferred in practice to take 100 c.c., and to contract the tube below this point, in order to get larger divisions, but I did not confine my apparatus to any such special form. On the contrary, I showed, even in my first communication, several modifications of the regulator (with cylindrical top, with bulb top, with tap, and with a capillary); I also said (*loc. cit.*, p. 444, line 24): "I quote, of course, these combinations, to be varied at will, merely as *examples* how the apparatus may be arranged," and in the *Zeitschrift für Angewandte Chemie*, 1880, pages 140 and 144, I remark that any "nitrometer (*a fortiori* any "gas burette") may serve the purpose of a regulator." Consequently, when he adopted for this purpose an ordinary 50 c.c. gas burette, Professor Japp did not introduce *any modification* in the principle of my "gas volumeter," but merely selected one out of the various forms which would at once occur to any chemist on reading my description, although certainly not that which admits, in my opinion, of the greatest accuracy in working. I think this explanation will suffice for the reconciliation of my two statements.

As already stated, I have objected to a new name being given to an instrument identical with the one invented and named by myself, except that the readings are taken in a new way; but since then I have met with another reason why the name "gravivolumeter" should not be applied to the instrument. That name was bestowed years ago by Houzeau on another instrument of totally different principles and use (*Compt. Rend.*, lxxxvii., 747; and xc., 870), and it would be likely to cause great confusion if designations previously proposed for totally different instruments were applied to new ones.

Professor Japp further says: "The acknowledgments of obligation throughout my entire note could hardly have been more profuse." But he seems to have overlooked the following passage at the end of my first paper in the *Berichte* in which: "*I reserve to myself the further extension of the principle embodied by my gas volumetor*, in this and in other directions, as well as the improvement in detail of the instruments shown here only in outline; but *I shall be grateful for any suggestions on the part of other scientists.*" In the *Zeitschrift fur Angewandte Chemie*, 1890, 142, more than a year before Professor Japp's first note, I repeated the above, adding that I intended to employ the name "gas volumeter."

Professor Japp admits that I have priority in the principle of reading off volumes of gases directly as weights, as when employing the gas volumeter for the estimation of nitrogen in organic combustions and for vapour densities. I had further claimed that I had attained the end of reading off volumes of gas directly as weights, by employing a certain weight of the substance to be analysed. To this Professor Japp objects that I do not find absolute weights, but merely percentage weights. Literally this is correct; but, as in almost all cases it is not the absolute but the percentage weights which are required, I fail to see the force of Professor Japp's objection.

I fully acknowledged the "sinnreiche Idee" of Professor Japp, which realises one of the "further extensions" of my principle foreshadowed in the above-mentioned

passage of my first paper; but I venture to submit, firstly, that it was not called for except in a limited number of cases; secondly, that it involved a loss of accuracy in the reducing operation. Both of these assertions I must maintain.

As for the first, I had already provided for all ordinary cases. In gas analysis proper, the reduction of volumes to weights is only quite exceptionally called for; in the gas-volumetric analysis of solid or liquid substances, the direct estimation of the percentage weight by my method is a distinct advantage over that of the absolute weights as shown above; and for the estimation of nitrogen and vapour densities it is necessary to employ, in lieu of gas burettes, specially constructed instruments, as described in my former papers.

According to my second criticism, Professor Japp's special form of regulator admits of only ½th (perhaps even ¼th) of the accuracy yielded by the form which I prefer. This he tries to refute by taxing me with ignorance of "a commonplace of physical measurement," namely, that there is no advantage in making one of the inter-dependent parts of a determination much more accurate than another; but he is in error, for he assumes that I generally work with a 50 c.c. gas burette, whilst, as a matter of fact, I prefer, wherever possible, to work with far greater volumes, for which purpose the gas burettes, as shown in my various papers, are constructed to hold up to 150 c.c. An uncertainty of 1/20th in 100 with the large gas burette is exactly the same as in my regulator, namely, 1/2000th, as against 1/500th, the probable error with Professor Japp's regulator, "calculated on the basis of 25 c.c. as the average amount of gas measured." By means of a small movable straight edge, combined with a spirit level (the description of which I shall shortly publish), I can attain such accuracy in levelling the mercury in both tubes that the above minimum of error is actually realised. Even with 50 c.c. of gas in the burette, the accuracy is—

$$\frac{1}{50 \times 20} = \frac{1}{1000}\text{th.}$$

This is, I think, sufficient refutation of Professor Japp's charge of ignoring "a commonplace of physical measurement."

I will lastly explain a passage in my note in the *Berichte* which Professor Japp seems to have misunderstood, the fault being doubtless attributable to the extreme conciseness of that note. I there said that by employing a volume of 25 c.c. only, in the regulator, the accuracy of reading is *a priori* reduced to ½th, and, on account of the inconvenient form of the tube, probably even to ¼th. The "inconvenient form" is that of a cylinder of equal width throughout as compared with that of an instrument bulged out at the top, in which only the bottom part is cylindrical and graduated, and the divisions may therefore be much larger than in the former case. In England, the bottom part need only hold 10 or 15 c.c.; at Zurich or Munich, 20 c.c. A 50 c.c. burette would have to be made very inconveniently long, if equally large divisions (easily readable to 1/40th) had to be provided.

*78. "*The Composition of Cooked Vegetables.*" By Miss K. J. Williams.

The vegetables examined after cooking were:—Artichoke (Jerusalem), broad bean, haricot bean, beetroot, cabbage, carrot, cauliflower, celery, cucumber, lettuce, mushroom, onion (Spanish), parsnip, pea (green), potato, radish, salsify, scarlet runner, sea-kale, spinach, tomato, turnip, and vegetable marrow.

Determinations were made in these of the following:—

Water.
Carbon and hydrogen.
Nitrogen (total) by Dumas method.
Nitrogen by soda-lime combustion.
Nitrate extracted by dilute alcohol.
Ashes.
Sulphur.
Woody fibre by digestion with dilute sulphuric acid, &c.
Cellulose by Schulze's potassium chlorate method.
Carbohydrate convertible into glucose.
Fat.
Heat of combustion.

The results are given in a series of tables.

Discussion.

Mr. Warington remarked that the determinations of the heat of combustion were of considerable value, as these were the only data on which, at present, a comparison of the relative values of the different foods could be based; to which Dr. Armstrong objected that the value of a vegetable food must depend both on the amounts of carbohydrates and albumenoids present and on their character, and therefore it did not seem probable that the determination of the heat of combustion would be of such special value. Mr. Warington then pointed out that the quantity of albumenoids required for the renovation of tissue in the human body was so small (at most 40 grms. per day) that it could hardly fail to be present in an ordinary mixed diet; unless, therefore, an increase were being made to the nitrogenous tissues, the value of a food practically depended upon the amount of heat which it could generate in the body, a remark which the Chairman subsequently said his experience of vegetarian diet enabled him to corroborate.

Dr. Kipping asked whether any attempt had been made to determine the effect on their composition of alterations in the mode of cooking vegetable foods.

Professor Ramsay, who had given an account of the paper, said in reply, that in his opinion more value would attach to the determinations of heats of combustion if the digestibility of the foods had also been ascertained. As to the influence of modes of cooking, considerable differences had been noticed by Miss Williams between potato boiled in the skin and without skin, but this was the only case hitherto studied.

*79. "*Metallic Hydrosulphides.*" By S. E. Linder and Harold Picton.

The authors have investigated the sulphides of copper, mercury, arsenic, antimony, cadmium, zinc, bismuth, silver, indium, and gold (*cf. Proc. C. S.*, 1890). With the single exception of bismuth, all these metals form hydrosulphides of a more or less complicated character, which, in most cases, undergo molecular condensation with elimination of sulphuretted hydrogen when submitted to the action of acids. Taking copper as a type, on treatment with sulphuretted hydrogen, copper hydrate forms a *solution* of the hydrosulphide $7CuS,H_2S$. Acetic acid, in presence of excess of sulphuretted hydrogen, promotes molecular condensation, a product being formed which has approximately the composition $9CuS,H_2S$; while acetic acid, in absence of sulphuretted hydrogen, promotes the formation of a product approximately represented by the formula $22CuS,H_2S$. Chlorhydric acid produces still further condensation. Mercuric sulphide forms products approximately represented by the formulæ $31HgS,H_2S$; $62HgS,H_2S$. The latter formula represents the precipitate formed in presence of acid, and is a remarkably stable substance. Zinc sulphide solution obtained from the hydrate contains about 14 per cent excess of sulphur as sulphuretted hydrogen; in presence of acetic acid, a product represented approximately by the formula $12ZnS,H_2S$ is formed.

The authors regard their results as evidence tending to support the conclusions that the metallic sulphides are in most cases polymerides of very high molecular weight.

*80. "*The Physical Constitution of some Sulphide Solutions.*" By Harold Picton.

The author has specially examined the solutions of mercuric, antimonious, and arsenious sulphides. In each case the whole of the dissolved sulphide is found to be present in the form of very finely divided particles.

Arsenious sulphide is found capable of existing in "solution" in three distinct types of sub-division. The following examples illustrate the main characteristics of sulphide "solutions":—

Mercuric Sulphide.—Particles are visible under the microscope (1000 diameters); is not diffusible even in absence of a membrane.

Arsenious Sulphide (α).—Particles are just visible.

Antimonious Sulphide.—Particles are not visible and it is not diffusible, but particles are detected by their power of scattering light, the scattered light being polarised.

Arsenious Sulphide (β).—Not diffusible; the particles scatter and polarise light.

Arsenious Sulphide (γ).—Diffusible in the absence of a membrane; particles are shown to exist by optical behaviour.

The solutions examined exhibit a series passing from those in which the particles of the solid are visible to those in which the particles simulate the phenomena of liquid diffusion, and, although not visible to the eye, are detected by their power of scattering light.

*81. "*Solution and Pseudo-solution.*" Part I. By Harold Picton and S. E. Linder.

The authors advance what they regard as a good *primâ facie* case for the belief that there is a continuous series of grades of solution passing without break from suspension to crystallisable solution. They hold that in the lowest grades of solution a certain loose attraction exists between the particles and the molecules of the solvent. This conclusion they support with experimental evidence gathered from their own work and from other sources. They regard the very finely divided particles in the lower grades of solution (colloid solution) as large molecular aggregates retaining many of their molecular properties. They consider that in passing up through the different grades of solution, these aggregates on the whole become smaller and the forces by which they are held in solution become more definitely those of chemical attraction. They describe a new property, which seems to hold for a large range of solutions, extending from suspension to crystallisable solution. This property consists in the repulsion of the dissolved substance, *as a whole*, from one of the electrodes of a battery immersed in the solution. Thus, in the case of colloidal arsenic sulphide, the sulphide aggregates are repelled from the negative electrode. They are also repelled, but much less strongly, from the positive electrode. In the case of the crystallisable colouring matter, Magdala red, in absolute alcohol, an exactly similar phenomenon is observed, but the repulsion is this time from the positive electrode, and there is no perceptible repulsion from the negative electrode at all. The property is of much interest in itself, but also as exhibiting similarities between the different grades of solution.

Discussion.

Mr. Page suggested that observations on the nature of solutions, such as those described by the authors, might with great facility be carried out in capillary tubes under the microscope.

Mr. Walenn said that in working with electro-coppering solutions containing resin in suspension, he had had occasion to notice a clearing of the liquid at the anode, such as had been referred to.

Professor Ramsay said that the problem of Brownian motion, or pedesis, had engaged his attention since 1878, when he published a paper in the *Proceedings of the Geological Society* bearing on the settling of mud in salt water. The problem attacked by Messrs. Linder and Picton was one in which he thought pedesis played an all-important part, as the small particles, the existence of which had been proved by their power of polarising light, were in exceedingly rapid motion. Messrs. Linder and Picton had shown that there is a regular transition from visible particles to particles or molecules such as those of oxyhæmoglobin. It must, therefore, be concluded that such exceedingly small particles are also in rapid motion; and the smaller the particles, the more rapid the motion. Pedesis had not received, as yet, any satisfactory explanation; the only fact which appeared to throw any light on its nature was that the addition of a salt to the solvent, rendering it an electrolyte, hindered pedesis, and finally caused coagulation and settling. The discovery of the true nature of pedesis would in all probability be the key to the problem of the nature of solution.

Mr. Warington pointed out that the coagulation of clay by salts had been studied by Schlœsing (*Chimie Agricole*, p. 62; Fremy's "Enclyclopédie," tome x; and W. Skey. Chem. News).

Mr. Herbert Jackson said that the phenomena discovered by the authors were similar to those observed in the case of the liquids produced during the washing of many precipitates, such, for instance, as lead hydrate or silver nitroprusside, which refuse to settle completely as soon as the liquid in which they are diffused becomes approximately pure water, or which show a tendency to come through the paper when washed on a filter. Such precipitates can be made to furnish turbid liquids in which the particles are so fine that they will not settle for many months, although, as is well known, the addition of a drop or two of a saline solution, *e.g.*, sodium acetate or potassium nitrate, will cause rapid deposition of the solid.

These opalescent liquids give the results described and shown by the authors when examined at right angles to a narrow beam of strong light.

He had found in the case of lead hydrate that the microscope revealed moving particles with an average diameter of 1/35,000 of an inch. Some, in the case of silver nitroprusside, were less than the 1/100,000 of an inch. The limit of separation with lenses and illuminators giving the greatest possible angle for water immersion (viz., 1·33 numerical aperture) is:—

For λ 5269	128,225	lines to the inch.
„ λ 4861	138,989	„ „
„ λ 4000	168,907	„ „

In the case of particles separated from one another by considerable intervals, these limits will be exceeded, as the dark diffraction outlines will give an apparent measurement of the particles distinctly greater than they really are; but it is quite clear that it is impossible to call a liquid homogeneous because the microscope fails to show structure.

All that can be said is that the particles in water, if not visible with lenses of the greatest possible angle for water, are probably not much greater than the 1/180,000 of an inch in diameter. Of course, it must be understood that changes in the limits will be observed when the refractive index of the particles differs very greatly from that of the fluid in which they are diffused, as is the case with As_2S_3 in water. It seems probable, therefore, that the phenomena observed in the cases of As_2S_3 and others which were mentioned, differ only in degree, and not in kind, from those in the cases of Sb_2S_3 and similar bodies, and from the opalescent liquids obtained in washing many precipitates.

*82. "*The Change Proceeding in an Acidified Solution of Sodium Thiosulphate when the Products are Retained within the System.*" By A. Colefax, B.A., Ph.D.

Experiments were carried out in the following manner:—A certain volume of a solution of sodium thiosulphate, acidified with an equivalent quantity of acid, was enclosed in a small glass bulb, from which the air had been displaced by carbon dioxide; several such bulbs were filled and placed in a bath at a fixed temperature, and at certain definite times after acidification the contents of a bulb was titrated by means of an iodine solution. The initial titration of the acidified sodium thiosulphate at the moment of acidification being known, the extent of chemical change is given by the iodine titration. The sulphurous acid resulting from the decomposition of thio-

sulphuric acid possesses a titration in terms of iodine the double of that of the undecomposed thiosulphuric acid. The possible sources of error are considered under the heads "Oxidation of sulphurous acid," "Titration complications," and "Incomplete saline decomposition." A further check is afforded by the determination of the acidity of the solution after the iodine titration is made. For a solution of sulphurous acid there is a constant ratio between the iodine titration and the acidity of the solution after the iodine titration has been made. This value was determined for the particular iodine and ammonia solutions by means of a pure solution of sulphurous acid. Hence, whether or not the whole of the increase in iodine titration in the acidified solution of sodium thiosulphate is due to sulphurous acid can be ascertained by a determination of the two values, iodine titration and acidity developed after titration with iodine.

The author concludes that the change proceeding in an acidified solution of sodium thiosulphate when the products, viz., sulphurous acid and sulphur, are retained in the system, is a reversible one: a limit being reached a certain time from the time of acidification. The value of this limit is affected by (1) state of concentration, (2) ratio of the mass of acid relative to the sodium thiosulphate, (3) the nature of the acidifying acid, (4) the temperature. Sulphurous acid cannot prevent the decomposition of thiosulphuric acid. The presence of both products of the change in the system seems essential for the attainment of a limit value; for sulphurous acid, when initially present in the system at the time of acidification, has but a small effect upon the values expressing the extent of chemical change. A higher temperature favours the interaction of sulphurous acid and hydrogen or sodium thiosulphate, a secondary change which proceeds at lower temperatures with extreme slowness.

Spring's statement that sodium trithionate is formed by the interaction of iodine, sodium sulphite, and sodium thiosulphate, seems to be wrong; the author finds that in adding to a solution of iodine a mixed solution of sodium thiosulphate and sulphite, no sodium trithionate is produced; the sodium sulphite is completely oxidised to sodium sulphate.

*83. "*The Action of Sulphurous Acid on Flowers of Sulphur.*" By A. COLEFAX, B.A., Ph.D.

Debus's statement that sulphurous acid has practically no action on sulphur is not confirmed. Sulphurous acid acts on flowers of sulphur at the ordinary temperature of the air, and produces thiosulphuric acid and a polythionic acid, probably trithionic acid. No pentathionic acid was found. According to Flückiger (*Jahresbericht*, 1863, p. 149), sulphurous acid gave, by its action on flowers of sulphur, thiosulphuric acid. The presence of a polythionic acid is proved by a comparison of the iodine titrations, and the acidity titrations before and after the addition of iodine requisite for the iodine titration. It is thus shown that there is present a considerable quantity of an acid having no iodine titration, and which is not merely oxidised sulphurous acid. Qualitative tests point to the presence of thiosulphuric acid, or trithionic acid, or a mixture of the two. Not even in the dark is sulphurous acid without action on sulphur. A higher temperature (say 80—90° C.) favours the action of sulphurous acid on sulphur; water has no action on flowers of sulphur, either at ordinary temperatures or at this higher temperature.

84. "*The α- and β-Modifications of Chlorobenzene Hexachloride.*" By F. E. MATTHEWS, Ph.D.

By the action of chlorine on chlorobenzene in presence of a dilute solution of sodium hydroxide, the author obtains a mixture of α- and β-chlorobenzene hexachloride, together with oily products which have not been investigated (*cf. Proc. Chem. Soc.*, 1890). The solid portion can be separated from the oily substances only with difficulty by pressure between filter-paper and washing with light petroleum. The α- and β-compounds are separated by means of steam distillation, the β-compound being much less readily volatile, and subsequent re-crystallisation from alcohol, benzene, or light petroleum.

α-$C_6H_5Cl_7$ is a colourless, crystalline substance, closely resembling α-benzene hexachloride in its properties; it melts at about 146°, and can be sublimed if carefully heated, but if heated too strongly, or on warming with an alcoholic solution of potassium hydroxide, it is quantitatively resolved into 1 : 3 : 4 : 5-tetrachlorobenzene and hydrogen chloride; on boiling an alcoholic solution with zinc-dust, chlorobenzene is obtained.

β-$C_6H_5Cl_7$ is only obtained in small quantity; it is more stable than the α-compound, and melts at about 260°; it is decomposed on heating either alone or with alcoholic potash, yielding the same tetrachlorobenzene as the α-substance.

Meunier's method of separating α from β-$C_6H_6Cl_6$ by means of an alcoholic solution of potassium cyanide has been investigated, and has been found to depend on the conversion of the α-$C_6H_6Cl_6$ into 1 : 2 : 4-$C_6H_3Cl_3$, the cyanide playing the part of a weak alkali.

1 : 3 : 4 : 5-$C_6H_2Cl_4$ has been investigated, with the result that the author is of opinion that the melting-point 50—51°, assigned by Beilstein and Kurbatow, is correct, and that Otto and Ladenburg, and Jungfleisch, who all give the melting-point considerably lower, were dealing with impure material. The nitro-derivative,—

$$C_6HCl_4(NO_2)(1:3:4:5:2),$$

was prepared and found to melt at 23° (Beilstein and Kurbatow, 21—22°).

The action of bromine on benzene in the presence of alkali has also been studied, and is found to yield $C_6H_6Br_6$, the product being the same whether gaseous or liquid bromine was used. On mixing monochlorobenzene with bromine under water and allowing the mixture to stand for about a week, a considerable amount of pure chlorobromobenzene was obtained.

The author calls attention to a paper by Sachse (*Ber.*, xxiii., 1363), in which Sachse shows that there are two positions of stability of the hexamethylene ring. According to Sachse's hypothesis, there should be two substances of the formula $C_6H_6Cl_6$ capable of existence, but three substances of the formula $C_6H_5Cl_7$, of which the two α-modifications would probably have very similar properties.

(To be continued.)

NOTICES OF BOOKS.

Methods of Gas-Analysis. By Dr. WALTHER HEMPEL, Professor of Chemistry in the Dresden Polytechnicum. Translated from the Second German Edition by L. M. DENNIS, Assistant Professor of Analytical Chemistry in Cornell University. Small 8vo., pp. 384. London and New York: Macmillan and Co.

IF we pronounce this work not merely good and useful, but even admirable, we shall not be guilty of exaggeration. There can be in these days no need to enlarge on the importance of gas-analysis whether for purely scientific or for technical work. English-speaking chemists will therefore, doubtless, gladly welcome the appearance of a version of this special manual prepared by so competent and experienced an authority as Dr. Hempel. The general principles of the art, the methods to be employed in working upon different substances, and the special precautions to be observed are given fully and clearly. The illustrations, 101 in number, are well drawn, and are selected so as to make the instruments and the operations fully intelligible.

The work consists of three parts, each divided into several chapters. The first part treats of general methods, such as the collecting and keeping of gases, the apparatus for technical gas-analysis, and that for exact gas-analysis

the arrangement and fittings of the laboratory, in which every precaution is duly explained. The second part embraces special methods. A comparison is given between the results of an exact analysis made over mercury and two partial analyses executed over water. The differences appear decidedly smaller than it might have been expected. Particular attention is given—as is quite justifiable—to the detection and determination of carbon monoxide. The most delicate method, however, is out of the reach of English chemists, as in it mice are employed. Hence the process would be denounced as "vivisection," and would subject the operator to severe penalties.

The author calls in question the assertion of Vogel and of Wolffhügel that proportions of carbon monoxide smaller than 0·25 per cent may be disregarded from a sanitary point of view. Decided symptoms of poisoning are produced in mice if 0·05 per cent of carbon monoxide are inhaled. He contends—and we unreservedly support his view—that the presence of any carbon monoxide should be regarded as inadmissible, so that heating appliances which allow it to mingle with the air of dwelling-rooms, workships, &c., are to be condemned.

Instructions are given for the examination of gun-cotton and nitroglycerin in a vacuum,—a very welcome improvement, as accurate analyses of these substances can rarely be obtained at the ordinary pressure of the atmosphere.

The determination of the heating-power of fuel is a subject which does not often figure in manuals of gas-analysis.

CORRESPONDENCE.

ESTIMATION OF FREE OXYGEN BY MEANS OF NITRIC OXIDE.

To the Editor of the Chemical News.

Sir,—It is matter of history that about a hundred years ago free oxygen was estimated by means of nitric oxide, and that by that method Priestley obtained results which were inaccurate and variable, whilst Cavendish obtained almost absolutely the same figures for the oxygen of the air as Bunsen and more modern observers who have employed the method of explosion in presence of excess of hydrogen gas. The question thence arose: How came it to pass that Cavendish could get correct results whilst other experimenters, operating by the same method and at the same date, obtained discordant and erroneous results?

As readers of the Chemical News who may have chanced to read our former communications will be aware, my colleague Mr. Cooper and myself have answered the question thus:—Under proper conditions—which admit of easy statement—the nitric oxide method answers perfectly, but when the proper conditions are not complied with, the method fails.

And in our little book entitled "Air Analysis" we have given very explicit directions for the performance of the analysis in question. From our publishers we learn that many hundred copies of our book are now in the hands of the public, and doubtless by this time we have a little army of experimenters who are ready to do battle for the honour of those fine old English chemists to whom we owe one of the easiest, most beautiful, and most accurate analytical processes in the whole range of chemical analysis.

Such being the case I am much amused by an attack upon us by L. L. De Koninck in the January number of the *Journ. Chem. Soc.*, of London (*vide* p. 97).

From Koninck's paper, as will be seen on reference to the Journal just mentioned, it would appear that in that gentleman's hands the nitric oxide process does not work at all. His results vary from 77·5 to 122·5 per cent of the amount of oxygen operated upon, and the difference between the process in our hands and in his is this: whilst he shows this wide variation, we show a variation of less than 1 per cent of the oxygen operated upon. In Koninck's paper he says that "the *modus operandi* was practically identical with that employed by Wanklyn and Cooper," and then proceeds to say explicitly what he really did.

In making the assertion that his *modus operandi* was practically the same as ours, Koninck has done himself an injustice. Cooper and myself do not claim for ourselves such superior manipulative skill that a *modus operandi* which in Koninck's hands is 25 per cent above or below the truth becomes less than 1 per cent distant from the truth in our hands. The difference is not so much in the skill of the operators as in the *modus operandi* itself.

In order that the reader may be in a position to judge of the importance of the differences between our *modus operandi* and that followed by Koninck, I will quote a passage from the preface to our "Air Analysis."

"The accuracy of modern technical processes of gas analysis has, we are aware, often been called in question. In particular it has often been said that measurements over water cannot be accurate because of the solubility of all gases in water. If in the Hempel apparatus the large bulk of liquid were boiled out so as to be devoid of air, there might be reason for the objection; but it is not, and therefore the error is restricted to that which arises from the difference of solubility of different gases. It is further to be noted that this error is eluded to a great extent, inasmuch as the contact between the gas and the liquids in Hempel's apparatus is too superficial to bring out these differences of solubility. In order to introduce serious solubility error, shaking up might be resorted to, and in that manner possibly some error might arise."

In Koninck's experiments the solubility error comes in in its worst and most exaggerated form; in our experiments the solubility error is avoided.

We welcome Koninck's paper as a warning to the readers of our book, who must not expect to succeed unless they follow our directions implicitly.—I am, &c.,

J. Alfred Wanklyn.

Laboratory, New Malden, Surrey.

METHYLATED SPIRIT.

To the Editor of the Chemical News.

Sir,—As regards obtaining unmineralised methylated spirit, it is less roundabout to make *direct* application to the Commissioners of Inland Revenue, Somerset House, London.

They, on receiving the application, will see that the proper officer deals with the matter. Your correspondent spoke of a £200 bond, but the Board of Inland Revenue do not, we are given to understand by Excise authorities, contemplate demanding this where less than 50 gals. is required per annum.

Our experience hitherto is that no one connected with a medical or scientific institution has been refused the power of obtaining unmineralised methylated spirit, provided that the element of retailing does not come in, and that he be able to order not less than five gallons at a time of a methylator, *not a retailer*.—We are, &c.,

A. and J. Warren,

Wholesale Druggists and Licensed Makers of Methylated Spirit and Finish.

23 and 24, Redcliff Street, Bristol, January 20, 1892.

THE DENSITIES OF SULPHURIC ACID.

To the Editor of the Chemical News.

SIR,—It is with regret that I find that any words of mine in your columns should have been considered by Prof. Lunge to be stronger than the circumstances of the case warranted, and I should have been pleased to apologise to him if he had traced his mistakes to any carelessness or ambiguity on my part. There is certainly much excuse for irritation when one finds a critic condemning a most laborious piece of work on the grounds that the very thing had been done which one had taken the greatest pains to point out to readers had *not* been done.

Prof. Lunge denied the accuracy of my determinations as far as their use in constructing a table was concerned by stating that I maintained the *actual* strength of the acid to be known to 0·001 per cent, and that I had obtained this result by analysis. The fact was, that I stated the strength to be known to 0·01 per cent, and that this result was *not* obtained by analysis. In excuse he now pleads that I gave the *relative* accuracy of the strength of the various solutions as 0·0001 per cent,—a value which, however, does *not* agree any better than 0·01 with his 0·001 per cent, and which, even if it did, could not be confounded with the *actual* accuracy,—and that in those tables which I used for the purposes of examining the results, I printed the strengths as given by analysis, stating, however, most clearly that these strengths were "712/1,000,000 too low."*

But what was or was not quoted in these tables is not to the point, for Prof. Lunge's remarks applied solely to the table of calculated values, and now that I have shown him that for the construction of this table the results of the analyses were *not* taken, and that neither the analyses nor the method used for determining the actual strengths were represented as giving the percentages correct to the "impossible" nicety of 0·001, and have thus removed the *only* objection which he raised against my work, he ought in "common fairness" (to use his own expression) to withdraw his opposition. It certainly appears strange to me that after I have now for the fourth or fifth time pointed out that the percentage values which I quoted had a relative accuracy of 0·0001 and an actual accuracy of 0·01, that Prof. Lunge should represent me (bottom of p. 13) as claiming "for them only a *relative* accuracy."

But Prof. Lunge seems fated to misrepresent me, for even in his communication to your journal he states that the method adopted by me for ascertaining the strength of the acid was "founded upon the hypothetical basis that the pure (acid) must have the lowest freezing-point." This would, indeed, be an hypothetical basis! What my method was founded on was that a pure substance has a *higher* freezing-point than an impure one, and this statement is based, not upon hypothesis, but upon fact. Out of the many thousands of cases which have been investigated there are only one or two in which the addition of impurity has been found to raise the freezing-point of a liquid, and the nature of the results with sulphuric acid can leave no doubt but that this substance does not form another instance of such abnormal behaviour.

I may add that Prof. Lunge's conjecture that Mr. Richmond made the same mistake as he did, and neglected my notification that the percentages given in my Tables I. to VI. were 712/000000 too low, is in direct contradiction to Mr. Richmond's statement that the values deduced by him agreed exactly with those given by me in Table VII., where the percentages are not 712/1,000,000 too low.—I am, &c.,

SPENCER PICKERING.

Harpenden, Jan. 9, 1891.

* In the paragraph which Prof. Lunge quotes in the CHEM. NEWS, vol. lxv., p. 13, he omits the sentence which comes after the word 'mentioned"; it is, "in all the other cases (*i.e.*, the cases in which the strengths quoted depended on analysis) the percentages quoted are 712/1,000,000 too low," a sentence which renders his conclusion that I accepted the analysis as giving the true strength of the acid entirely untenable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 1, January 4, 1892.

The past year has brought many changes in the Academy. Among the members Edmond Becquerel, M. Cahours, and Alfred Richet are dead. Of its foreign associates the Academy has lost the ex-Emperor of Brazil, and of its correspondents MM. Kronecker, Boileau, Ibañez de Ibero (Marquis de Mulhacen), Weber, Stas, De Andrade Corvo, and Palasciano. Seven vacancies remain to be filled.

Remarks on the Mechanism of the Fixation of Nitrogen by Soil and Plants with reference to the Reply of MM. Schloesing, jun., and Laurent.—Arm. Gautier and R. Drouin.—A brief controversial note.

Direct Combination of Nitrogen with the Alkaline Earthy Metals.—M. Maquenne.—Hitherto we have only known a small number of metals capable of directly fixing nitrogen in notable proportions, and those which, like magnesium and aluminium, form definite nitrogenous compounds, manifest this property only at white redness. The author finds that the alkaline earthy metals give rise to the same reaction at a cherry-red heat, forming nitrides which are immediately decomposable by water with production of ammonia. The author's process consisted in heating a rich amalgam of the metal studied (15—20 per cent), in an atmosphere of pure dry nitrogen. The experiment must be made in a boat of iron or nickel as platinum is rapidly attacked. The temperature is kept at dull redness for half an hour so as to expel the greater part of the mercury. It is then raised for a few instants to bright redness and let cool. The nitride appears as a brown mass of a semi-metallic lustre, very easily attacked by moist air. The experiment succeeds most readily with barium. If the nitride is brought in contact with water hydrogen is evolved whilst ammonia remains in solution. The result is obtained in the entire absence of carbon.

Nitration of the Hydrocarbons of the Methane Series.—M. Konovaloff.—The normal hydrocarbons of the methane series may be nitrised by the action of weak nitric acid, and yield secondary nitro-products as principal products. Secondary nitro-hexane and nitro-heptane yield by the action of nitrous acid a colouration indicating the probable formation of pseudonitrole. On the reduction of these nitro-products we obtain corresponding amines and ketones.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Medical, 8.30.
—— Society of Arts, 8. "Developments of Electrical Distribution," by Prof. George Forbes, F.R.S.
TUESDAY, 26th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "The Woodcuts of Gothic Books," by William Morris, M.A.
—— Royal Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.
WEDNESDAY, 27th.—Society of Arts, 8. "The Scientific Value of Lovibond's Tintometer," by F. W. Edridge-Green.
THURSDAY, 28th.—Royal, 4.30.
Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Some Aspects of Greek Sculpture in Relief," by A. S. Murray.
FRIDAY, 29th.—Royal Institution, 9. "Tales of the Scottish Peasantry," by Sir George Douglas, Bart., M.A.
SATURDAY, 30th.—Royal Institution, 3. "The Induction Coil and Alternate Current Transformer," by Professor J. A. Fleming, M.A., D.Sc.

ERRATUM.—P. 27, col. 2, line 3, *for* "Brown" *read* "Blown."

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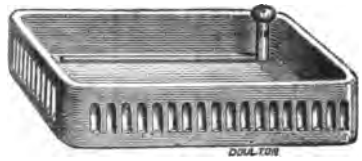

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Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents, issued on the 6th January, 1892.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment, within one calendar month from the date of the said Journal.

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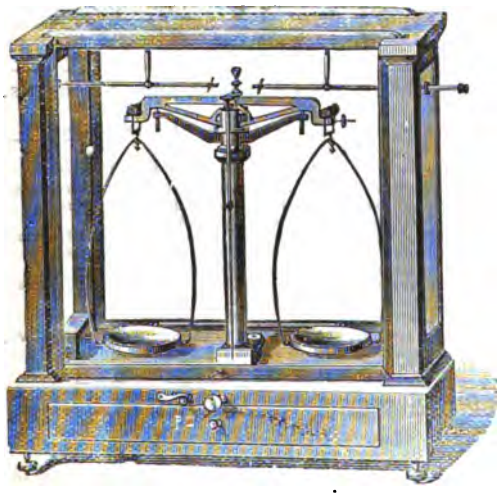

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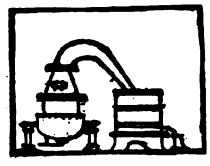

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THE CHEMICAL NEWS.

Vol. LXV., No. 1679.

NOTES FROM FLORIDA ON THE GLASER METHOD FOR THE DETERMINATION OF IRON AND ALUMINA.

By BEVINGTON H. GIBBINS, F.C.S., Ocala, Fl.

It is a curious fact that in all the literature bearing on the Glaser method for the determination of iron and alumina oxides, which has been published in the past year or two, no further reference has been made to the suggestion of Messrs. Teschemacher and Smith in the Chemical News, vol. lxii., p. 84. The addition of ammonia to the alcoholic acid solution of the phosphates is there recommended previously to the expulsion of the alcohol. The writer adopted this course of procedure at the time of its publication, and has never found it otherwise than satisfactory when certain precautions are observed.

It is, of course, obvious that if a large excess of ammonia is here added, magnesia, if present, will most certainly be deposited as magnesium ammonium phosphate. That this is not the case when ammonia is added carefully with only a drop or two in excess, any operator can easily prove for himself by adding a large excess of magnesium oxide to a sample of phosphate of known composition. On putting such a mixture through the Glaser process, a precipitate of phosphates of iron and alumina is obtained in due ratio to that in the original phosphate, which can easily be proved to be free from magnesia. The writer has obtained this result when 25 per cent of magnesia was added.

Daily experience for over a year has shown that the simplest and cleanest way to conduct the operation is to place the aliquot portion of the alcoholic acid solution in a porcelain dish, and then to add ammonia of specific gravity 0·96 from a burette, with constant stirring. Testing with a strip of litmus paper answers well. If the ammonia is too strong, a partial separation of the alcohol takes place, rendering it difficult to hit the point of neutrality. When neutral the dish is placed on a steam bath, and in about three quarters of an hour the alcohol has usually disappeared. It is essential not to carry this evaporation to dryness, as, if the silica has not been completely eliminated previously, it will here be rendered insoluble. The contents of the dish are then washed out into a beaker, a few drops more ammonia added, and boiled thoroughly. Then, if it is cooled rapidly by placing the beaker in a pan of water, immediate subsidence ensues, and filtration may be proceeded with without delay.

I have found this method far more rapid than the evaporation of the alcohol from the acid solution, and the disagreeable results of the exposure of any organic matter to the action of sulphuric acid, and subsequent necessity for oxidation with bromine, are entirely avoided.

If ammonia of specific gravity 0·89 is added to the alcoholic acid solution, complete separation of the solution into two layers is noted, the alcohol being all contained in the upper layer, and the precipitate in the lower one. It was a question at one time in my laboratory whether the alcohol could not be thus eliminated by means of a separatory funnel, but in view of the fact that evaporation occupies less than an hour, and that other work can very conveniently be sandwiched in at this juncture, the idea was relinquished.

In some samples of Florida phosphates manganese is present to an appreciable extent. It is noticed in nearly all sample of the gravel which is found adjacent to the deposits of "plate rock," and which is usually mixed with the "plate rock" in cargoes. In some instances I have picked out concretions of pyrolusite one-eighth of an inch in diameter, but it more often occurs in thin layers, and is with difficulty detached from the phosphate.

When manganese is present the precipitate of phosphates of iron and alumina will be found contaminated with it. In such cases, if the precipitate is, after partial washing, re-dissolved in dilute nitric acid, a little phosphate of ammonia added to the solution, and then ammonia until neutral, a second precipitate is obtained free from manganese. I should advocate this course in all samples of gravels and plate rock. I have never detected manganese in samples of boulder phosphate, nor in the pebble deposits of South Florida. The gravels referred to usually contain from 73—78 per cent of phosphate of lime, and can never be mistaken by anyone who has once seen them in the unground condition.

SEPARATION OF ARSENIC AND OF PHOSPHORIC ACID FROM MERCURY, AS ALSO DETERMINATION OF NITRIC ACID, CHLORINE, AND SODIUM, IN PRESENCE OF MERCURY AND PHOSPHORIC OR ARSENIC ACID.

An Inaugural Dissertation.

By KONRAD HAACK.

For the separation of arsenic acid from mercury, present in the mercuric state, the substance is dissolved in a little hydrochloric acid, the solution is supersaturated with ammonia, and to the white precipitate thus formed there is added drop by drop a clear solution of potassium cyanide, not very dilute, until the white precipitate is completely re-dissolved. The solution is then first mixed with so much ammonia as amounts to one-fourth of the entire volume of the solution, and then with the same quantity of absolute alcohol. The arsenic acid is then precipitated in the ordinary manner, and in the filtrate which is slightly acidulated and diluted, the mercury is thrown down by sulphuretted hydrogen.

If the mercury is present in the mercurous state the substance is dissolved in a little nitric acid, a little hydrochloric acid is added, and a few particles of potassium chlorate, and the liquid is heated on the water-bath until it becomes clear and no longer smells of chlorine, proceeding afterwards as above.

Before applying this method of separation, the author had followed Rose's method, throwing down the mercury from the hydrochloric solution of the substance by means of phosphorous acid as mercurous chloride. The results, however, were never accurate, as the precipitation of the mercury was never complete even after standing for several days.

2. The separation of phosphoric acid from mercury is effected exactly in the same manner. The results are quite as accurate as by the sulphuretted hydrogen method.

3. The determination of nitric acid in presence of mercury and arsenic acid, or phosphoric acid, is founded upon the fact that a solution of barium hydroxide completely decomposes the metallic nitrates.

The solid substance is boiled for about fifteen minutes with a solution of pure barium hydroxide in excess. It is filtered whilst hot, and washed with hot water until baryta can no longer be detected in the washings. The filtrate contains the nitric acid as barium nitrate, and in addition barium hydroxide.

There is then passed into the filtrate a current of carbonic acid to remove the barium hydroxide until the alkaline reaction has disappeared. It is then boiled for half an hour to expel free carbonic acid, filtered whilst hot, and washed with hot water. The second filtrate, which contains merely barium nitrate, is largely diluted, and dilute sulphuric acid is added. From the weight of the barium sulphate precipitated the nitric acid present may be readily calculated.

If, in the substance containing the nitric acid, there is present beside mercury and arsenic—or nitric acid—an alkaline metal, the quantity of nitric acid present can be determined by this method only if the alkali present does not suffice to convert all the nitric acid into nitrate of alkali, and if the quantity of the alkali itself is already known. Only that part of the nitric acid is taken up by the baryta which the alkali does not suffice to combine with. The nitric acid united with the alkali cannot be determined but merely calculated.

4. For determining chlorine in presence of mercury and arsenic acid, or phosphoric acid, the solid substance is boiled for fifteen minutes with an excess of solution of baryta and filtered. The precipitate, after washing, contains no chlorine, and the filtrate no mercury. In the filtrate the chlorine is determined after acidulation with nitric acid in the usual manner as silver chloride.

5. For determining sodium in presence of mercury and phosphoric acid, the hydrochloric or nitric solution of the substance is mixed with baryta water until the reaction is slightly alkaline and then boiled for fifteen minutes. It is then filtered and washed until free from baryta. In the precipitate are found the mercury and the phosphoric acid, whilst the solution contains all the sodium, barium hydroxide, and barium salts.

After the baryta has been precipitated with sulphuric acid in the boiling solution previously acidified, and after the precipitate has been filtered off, the filtrate is first concentrated in a platinum capsule and then evaporated completely to dryness in a tared crucible. From the weight of the ignited residue, which consists of sodium sulphate, the proportion of sodium in the substance is known.

6. The determination of sodium along with mercury and arsenic acid is effected by heating the substance gently in a tared porcelain crucible along with solid ammonium chloride, until the weight is constant. The residue is taken as sodium chloride.

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.

By CH. MALOT.

The phosphoric acid is first separated in the well-known manner as ammonium phosphomolybdate, the precipitate is dissolved in ammonia, and re-precipitated with magnesia mixture. After filtration the ammonium-magnesium phosphate is dissolved upon the filter in nitric acid of specific gravity 1·2, and the phosphoric acid is determined volumetrically with a solution of uranic nitrate. In this titration the author evades the spotting test with potassium ferrocyanide for detecting the end of the reaction by making use of tincture of cochineal, and of the property of uranium oxide to form a green lake with the colouring matter of cochineal. The nitric solution is mixed with a few drops of tincture of cochineal (obtained by treating cochineal with boiling water), an excess of the tincture being avoided, as a too intense colour interferes with the sensitiveness of the reaction. Ammonia is then added to the solution until a permanent violet colour is produced, and this colour is again removed by the addition of a drop or two drops of nitric acid.

He adds further 5 c.c. of a solution of sodium acetate (containing per litre 100 grms. of the salt), and then 50 c.c. of glacial acetic acid, heats to 100°, and titrates the hot solution with a neutralised solution of uranium nitrate of known efficacy. Each drop of this solution produces in the liquid mixed with cochineal tincture a greenish-blue spot the further the precipitation has advanced. It disappears on shaking, and the rose colour of the cochineal re-appears until the precipitation is complete.

As soon as all the phosphoric acid has been precipitated by the solution of uranium nitrate, the liquid takes a bluish-green colour, which is not affected by any further addition of uranium nitrate. If a drop of the solution is brought in contact with a particle of ferrocyanide there ensues no colouration; in order to produce a distinct brown colour a little more of the uranium nitrate solution must be added.

It is convenient to use a solution of uranium, of which 1 c.c. corresponds to 2 m.grms. phosphoric acid, and standardised to a solution of phosphoric acid of known strength, carefully observing the above conditions and heating the solution to 100°.

The results obtained by Malot, according to this method, always agree to $\frac{1}{10}$ c.c. or $\frac{1}{2}$ m.grm. phosphoric acid. As the method, in addition to its accuracy, is very expeditious, the author prefers it both to the "spotting" test with ferrocyanide and to the direct weighing of the magnesium pyrophosphate.—*Zeit. Anal. Chemie.*

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To General A. De Courcy Scott, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, January 9th, 1892.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 166 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 166 samples examined, 160 were found to be clear, bright, and efficiently filtered. Four were recorded as "slightly turbid" (S.T.), and two as "very slightly turbid" (V.S.T.).

Although the generally turbid and flooded condition of the rivers throughout November was appreciably exceeded during the following month by reason of the heavy rainfall, the state of the December water supply showed upon the whole a distinct improvement. Thus, taking the Thames-derived supply for comparison, the mean degree of colour-tint was found to be reduced from 22·1 : 20 to 18·7 : 20; the mean amount of oxygen expended in oxidation from 0·101 grain per gallon to 0·079 grain; the mean

amount of organic carbon from 0·250 to 0·240 part in 100,000 parts; and the maximum amount of organic carbon in any single sample examined from 0·391 part to 0·319 part. Similarly, in the case of the New River and East London Companies' supplies for the two months respectively, the results obtained during December showed a similar improvement over those recorded in our previous month's report.

We are, Sir,
Your obedient Servants,

William Crookes.
William Odling.
C. Meymott Tidy.

ON A

RAPID METHOD FOR THE ACCURATE RECOGNITION OF SULPHIDES, ARSENIDES, ANTIMONIDES, AND DOUBLE COMPOUNDS OF THESE BODIES WITH METALS.*

By CHARLES A. BURGHARDT, Ph.D., &c.

(Concluded from p. 44).

Antimony Sulphide.

Stibnite, Sb_2S_3.—Fused in the same kind of apparatus as that used for the sulphides of arsenic, yielded sulphuric acid in the water and a mixture of Sb_2O_3 and Sb_2O_5. A little sulphuric acid was also detected in the water which had been used to boil the residue in the fusion tube. On adding a solution of potassium bisulphate to the residue in the fusion tube, and a piece of pure metallic zinc, antimoniuretted hydrogen was at once evolved, and a mirror of metallic antimony obtained on heating the delivery tube to redness. Other tests applied proved this mirror to be really antimony. The mineral did not give reactions for any other element likely to be present, hence it was sulphide of antimony.

If it is suspected that both arsenic and antimony are present in a mineral in large amount, they can be easily separated from each other by substituting sodium nitrate for ammonium nitrate, when a compound of antimony and sodium, insoluble in cold water, is obtained (antimoniate of sodium), whilst the arsenic forms arsenite and arsenate of sodium, both of which are soluble in cold water after standing some time.

Löllingite.

$FeAs_2$—Fused with ammonium nitrate in a platinum crucible or porcelain crucible. Melt, red coloured. Dissolved in hot water gave the reactions for arsenious and arsenic acid with silver nitrate and the usual arsenic reactions. The insoluble residue gave the reactions for iron. The mineral was therefore an arsenide of iron.

Proustite.

Ag_3AsS_3.—Fused in the same manner as the last-mentioned mineral, yielded a black residue containing arsenic oxide (this residue will be the subject of special examination, as it is peculiar). The melt was treated to separate the black residue. A solution of silver sulphate was obtained, which gave the characteristic reactions for silver and sulphuric acid. The black residue was treated with the acid potassium sulphate solution and metallic zinc, and arsenic was detected in the usual manner. The solution in water also gave the characteristic reaction for arsenic acid with silver nitrate. All the silver of the proustite was converted into sulphate, on account of the high percentage of sulphur in this mineral. The mineral was therefore a sulph-arsenite of silver.

Pyrargyrite.

Ag_3SbS_3.—Treated in the same way as the preceding mineral, sulphate of silver was obtained in solution in water, and insoluble antimonious and antimonic oxide (Sb_2O_3 and Sb_2O_5) remained as a residue. The antimony reactions were obtained, and only silver and sulphuric acid detected; consequently, the mineral was a silver sulph antimonite.

Argentite.

Ag_2S.—On treating this mineral in the same manner as pyrargyrite, sulphate of silver was produced in small amount, owing to the small percentage of sulphur present in argentite. On adding a small quantity of "flowers of sulphur" to the powdered mineral, and then fusing the mixture with the ammonium nitrate, a larger quantity of silver sulphate was obtained. The solution gave the reactions for silver and sulphuric acid only; consequently, the mineral was a sulphide of silver.

Iron Pyrites.

Marcasite. Pyrites. FeS_2.—Fused as above, gave a reddish brown residue of ferric oxide, Fe_2O_3, and a brown solution in water, which gave the characteristic reaction for ferric salts with potassium ferrocyanide solution, and also the reaction for sulphuric acid. The mineral was therefore sulphide of iron.

Galena.

PbS.—Gave a white residue (insoluble in water) of lead sulphate, and nothing in solution. The residue was dissolved in hot hydrochloric acid; when a portion of the solution gave a white precipitate (of barium sulphate) on the addition of a solution of barium nitrate, and another portion of the hydrochloric acid solution, on being neutralised with sodium carbonate and boiled with a solution of potassium bichromate, gave the characteristic yellow lead chromate reaction. The white lead sulphate residue mentioned above, on being treated *directly* with the solution of potassium bichromate, also gave the lead chromate reaction. The mineral was therefore a sulphide of lead.

Copper-glance (Redruthite).

Cu_2S.—Gave a blue melt whilst hot, which became brown on cooling. The melt dissolved completely in water into a blue solution, which gave the usual reactions for copper and sulphuric acid. The mineral was therefore a sulphide of copper.

Bismuth-glance.

Bi_2S_3.—The melt was brown when cold. A solution of sulphate of bismuth was obtained, which gave the reactions for bismuth and sulphuric acid. An excellent and delicate reaction for bismuth is that which was shown to me by Professor Bunsen, at Heidelburg, twenty-one years ago, which I have never yet seen described in any work on qualitative analysis. In applying it to the solution of the melt first add a slight excess of caustic soda solution to it, when a white precipitate of hydrated bismuthic oxide ($Bi_2O_3H_2O$) is obtained. In another vessel add an excess of caustic soda solution to a solution of stannous chloride, when a white precipitate of hydrated stannous oxide ($SnOH_2O$) falls out, but immediately re-dissolves in the excess of caustic soda. The bismuth precipitate obtained as above is washed into a white basin and a portion of the caustic stannous solution poured upon it and well stirred with it, when very soon a dense black precipitate is seen in the white basin, this precipitate being an oxide of bismuth, Bi_2O_2, formed by the reduction of the Bi_2O_3 through the SnO.

Millerite.

NiS with Co and Fe.—Gave a green solution of sulphate of nickel, which gave the characteristic reactions for nickel and sulphuric acid, and also those for cobalt and iron. There was an insoluble brown residue of ferric oxide from the melt. The mineral therefore was a sulphide of nickel.

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* From the *Mineralogical Magazine*, Vol. ix., No. 43.

Copper Pyrites.

$CuFeS_2$.—Gave the same reactions as those obtained in the case of chalcocite *with the addition* of a copious reddish brown insoluble residue from the melt of ferric oxide. The solution of the melt in water was blue. The melt in the crucible was reddish brown. The mineral was therefore a sulphide of copper and iron.

Bournonite.

$CuPbSbS_3$.—Melt after fusion yellowish green. Treated with water gave a solution of copper sulphate, in which both copper and sulphuric acid were detected as in chalcocite, &c. The insoluble residue (after dissolving out all the copper sulphate) was found to be sulphate of lead and antimonious and antimonic oxides. A portion of this insoluble residue was treated with acid sulphate of potassium (as in stibnite), when all the antimony was eliminated as antimoniuretted hydrogen, and the residue of lead sulphate treated as the sulphate of lead obtained from galena, and the presence of lead demonstrated. The mineral therefore was a copper-lead sulph-antimonite.

Tetrahedrite, or Fahl-ore.

$Cu_8Sb_2S_7$.—The melt was green whilst fusing, but brown when cold. Treated with water gave a blue solution of copper sulphate, ferric sulphate, and traces of zinc sulphate and arsenious acid. The usual tests were applied to this solution, and copper, iron, and sulphuric acid detected.

The residue insoluble in water was found to be antimonic oxide (Sb_2O_5) and ferric oxide. On boiling the residue with caustic potash, the Sb_2O_5 was dissolved and the ferric oxide remained. On adding hydrochloric acid in excess to the antimonate of potassium and a piece of metallic zinc, antimoniuretted hydrogen was detected in the way described above. The mineral therefore was a copper-iron, &c., sulph-antimonite.

Smaltite.

$(Co, Fe, Ni)\ As_2$.—The melt was pink whilst fusing. Treated with water and boiled, an insoluble residue of cobalt, iron, and nickel oxides remained, whilst arsenious acid passed into solution, and the arsenic was detected in the usual manner. The oxides of the metals thus obtained were dissolved in hydrochloric acid and tested chemically for cobalt and nickel, also iron, and these metals were detected.

Where arsenic and antimony combine with metals forming antimonides and arsenides, and no sulphur is present, oxides of the metals are obtained together with oxides of antimony and arsenic. By adding sulphur to these compounds, the metals are converted into sulphates and become soluble.

I have still to discover a good method for the separation and detection of cobalt and nickel, suitable for mineralogical analysis.

In conclusion, I must acknowledge the great assistance I have received from my assistant, Mr. Gilbert Rigg, in this investigation.

Note.— Since writing the above I have made some further experiments, and have succeeded in separating cobalt from nickel in the most complete manner. If the mineral is an arsenide or antimonide of cobalt and nickel it is fused as described in the treatment of smaltite, and when all the metals are converted into oxides a lump of ammonium nitrate is added to the melted mass from time to time, and the whole is kept gently simmering for three or four minutes. The melted mass assumes a pink colour due to the formation of nitrate of cobalt. After cooling, the melt is boiled out with water; NiO remains behind absolutely free from CoO. The cobalt nitrate solution is evaporated to dryness in a porcelain basin and ignited at about 250° C., when all the ammonium nitrate present is volatilised and pure pink cobalt nitrate remains in the basin. If the mineral is a sulphide of nickel and cobalt, fuse it with 10 per cent of its weight of powdered carbon (previously added to the powdered mineral), and about four times its weight, or more, of caustic soda in a silver crucible. Sodium sulphide is produced, and dissolved out by water from the cooled melt, and the oxides of cobalt and nickel remain behind; they are then treated with ammonium nitrate as described above.—C. A. B.

THE OXIDATION OF METALLIC ARSENIDES BY THE ELECTRIC CURRENT.*

By LEE K. FRANKEL.

The decomposition of minerals and their subsequent oxidation by means of the electric current is a product of very recent origin. By reference to the literature of the subject, it will be found that the first attempt in this direction was made by Dr. Smith, in a paper published in the *Proceedings* of the Chemical Section of the Franklin Institute, vol. i., p. 52, in which the author has successfully completed the decomposition of chalcopyrite, and gives the results of some preliminary investigation on chromite.

In a later and more exhaustive paper in the same journal, Dr. Smith has published his researches on the decomposition of other sulphides, and has proven conclusively that oxidation by the electric current gives results as quantitatively correct as those obtained by any wet or fusion method. In a still later paper by the same author (*Amer. Chem. Journ.*, vol. xiii., No. 6), experiments on various kinds of chromite indicate that the decomposition of this mineral is complete, if the conditions prescribed are closely followed. At present this completes the literature of the subject, and judging from the success so far obtained, it was deemed advisable to attempt the oxidation of the metallic arsenides, with the hope that the result would be similarly fruitful. These results and the methods used for obtaining them will be found appended below.

The apparatus used for this purpose was the same as that described by Dr. Smith in the *Proceedings* of the Chemical Section of the Franklin Institute, vol. ii., p. 53, and the method of using it was also substantially the same. The current generated from four storage cells of the Julien type was passed through the resistance frame, then through a Kohlrausch ampèremeter, and lastly up through the nickel crucible, the latter being in all cases the positive pole. As for the oxidations, the time required, the strength of current, &c., differed in each mineral respectively. For this reason no general plan can be prescribed, but the details of the work will be found for each mineral under its respective heading.

Gersdorfite (*Ni.Fe.*), *As.S.*—The sample used for the decomposition came from Shladming. The method of procedure was as follows:—In a nickel crucible 1¼ inches high and 1⅛ inches wide, 25—30 grms. of solid caustic potash were placed. The contents of the crucible were heated until fusion took place, and the gersdorfite then carefully added. A current registering 1 ampère was passed through the mass for twenty minutes, the crucible being the anode. Towards the end of the operation the current was reversed for three minutes to remove any particles of mineral that might have been enclosed in the metal deposited on the cathode. After breaking the current the crucible was allowed to cool, then thoroughly disintegrated with water, and the resultant insoluble material (nickel and iron oxides) filtered off. The clear filtrate was acidulated with concentrated hydrochloric acid, and then made strongly alkaline with ammonium hydrate. The precipitate (silica and alumina from the

* Read at a meeting of the Chemical Section of the Franklin Institute, November 17, 1891.

caustic potash), which formed on the addition of the latter reagent, was filtered off, and magnesia solution added. The precipitate of magnesium ammonium arseniate which formed after standing twelve hours was filtered off, dissolved in dilute hydrochloric acid, re-precipitated with ammonium hydrate, filtered, dried, weighed, and ignited in a platinum crucible in the manner prescribed for this determination. The results obtained were as follows:—(1) 0·2777 grm. of ore gave 0·2853 grm. of magnesium pyroarseniate = 49·73 per cent arsenic; (2) 0·1137 grm. of ore gave 0·1173 grm. of magnesium pyroarseniate = 49·94 per cent arsenic; (3) 0·2548 grm. of the ore was dissolved in nitric acid, evaporated to dryness, the residue taken up in hydrochloric acid, and the arsenic acid reduced with sulphurous acid. Hydrogen sulphide was then added, the resulting arsenious sulphide filtered off, dissolved in nitric acid, the solution made alkaline with ammonium hydrate, magnesia mixture added, and the arsenic determined as above; 0·2617 grm. of magnesium pyroarseniate was found = 49·72 per cent arsenic.

The insoluble residue remaining after the fusion was dissolved in water was treated with nitric acid and evaporated to dryness. Hydrochloric acid was then added, and hydrogen sulphide passed through the solution for several hours, without the formation of any precipitate of sulphide of arsenic, showing that the mineral must have been completely decomposed.

Niccolite (*Ni.As.*).—With this mineral the attempt was made to see what effect currents of greater intensity would have on the decomposition. It was hoped that with a current of greater strength the decomposition could be effected in less time, but as will be seen, the results, as far as a diminution of the time limit is concerned, are practically negative.

Two samples of the finely-ground niccolite were subjected to a current which varied from 1½—1¾ ampères for twenty minutes, and without any reversal of the current, 25—30 grms. of caustic potash being used. In both cases did the residues which remained after disintegrating the fused mass with water show the presence of arsenic, on treating the residues with nitric acid, evaporating to dryness, and the subsequent addition of hydrochloric acid and hydrogen sulphide. The presence of arsenic in the residues is probably due to the fact that the greater strength of current used in the decomposition deposits larger quantities of metallic nickel on the cathode, enclosing at the same time appreciable quantities of undecomposed mineral.

A much weaker current was now tried. Two samples of the mineral were subjected to a current of half an ampère for twenty minutes, 25—30 grms. of caustic potash being used. The result was the same as in the previous case, arsenic being found in both of the residues.

The time limit was now extended with more satisfactory results, the manner of decomposition being as follows:—A current of 1 ampère was allowed to pass through the fused mass for twenty-five minutes, the current passing up through the crucible. At the end of this time the current was reversed for five minutes to remove the metal and any undecomposed mineral that may have attached itself to the platinum wire. The subsequent operations of extracting the alkaline arseniate and weighing it as magnesium pyroarseniate were similar to those already given under gersdorfite, with the exception that instead of filtering the precipitation of magnesium ammonium arseniate through filter-paper, and igniting it in a platinum crucible, the precipitate was filtered directly through a porcelain Gooch crucible, of the pattern recommended by Prof. Caldwell. Owing to the fine, granular condition of the precipitate, this requires some care, particularly if the filter-pump be used. The best results were obtained by first placing a layer of glass wool in the crucible and covering this with a layer of asbestos. After filtering, the crucible with its contents was first dried on a hot plate until all moisture was removed, and then gradually heated over a Bunsen burner for an hour. In this time all the precipitate will be converted into magnesium pyroarseniate. It is hardly necessary to state that the flame from the burner should not be allowed to enter the crucible below, lest a partial reduction of the precipitate ensue. It was also found advisable to allow the crucibles to stand for twelve hours after ignition, since the constant change in temperature made appreciable differences in the weighings. The results were as follows:—0·1209 grm. of niccolite gave 0·1301 grm. of magnesium pyroarseniate = 52·09 per cent arsenic; 0·1540 grm. of niccolite gave 0·1672 grm. of magnesium pyroarseniate = 52·55 per cent arsenic.

The residues left after disintegrating the fusions gave no reactions for arsenic. They both had a peculiar crystalline appearance resembling minute plates. They dissolved in nitric acid without any evolution of nitrous fumes, and are probably oxide of nickel.

Another sample of the ore was dissolved in nitric acid, the excess of acid evaporated, ammonium hydrate added along with magnesia solution, and the arsenic determined in the usual manner as magnesium pyroarseniate, the weighing being made in a platinum crucible, with the following result:—0·2611 grm. of niccolite gave 0·2833 grm. of magnesium pyroarseniate = 52·52 per cent arsenic.

Arsenopyrite (*Fe.As.S*).—The conditions under which arsenopyrite is decomposed are very similar to those of niccolite. The quantity of caustic potash used, the time of decomposition, the reversal of the current, &c., are precisely the same, the only difference between them lying in the fact that in the decomposition of arsenopyrite it was found that the current might vary from 1—1¼ ampères without affecting the decomposition. The method of determining the arsenic, as far as the Gooch crucible, &c., is concerned, was the same as under niccolite. Results as follows:—

0·2168 grm. of arsenopyrite gave 0·1729 grm. of magnesium pyroarseniate = 38·6 per cent arsenic.

0·1709 grm. of arsenopyrite gave 0·1356 grm. of magnesium pyroarseniate = 38·41 per cent arsenic.

The residues from the fusions, treated similarly to those under niccolite, showed no traces of arsenic.

0·2306 grm. of the ore were dissolved in concentrated nitric acid, evaporated to dryness, treated with hydrochloric acid and water, and any insoluble matter remaining filtered off. The solution was then reduced with sulphurous acid, the excess removed by boiling, and the arsenic precipitated by hydrogen sulphide. The solution was then allowed to stand until the odour of hydrogen sulphide was barely perceptible, and then filtered on a porcelain Gooch crucible, washed with cold water, carbon disulphide, and alcohol, dried at 100° C. and weighed. The result was 47·73 per cent As. As the high result could be due to but one cause, viz., the presence of sulphur in the precipitate, repeated treatments with carbon disulphide and alcohol were given the latter, but without avail. The precipitate was eventually dissolved in nitric acid, and the arsenic thrown out with magnesia solution. Found: 0·1856 grm. of magnesium pyroarseniate = 38·96 per cent arsenic.

It will be seen from this that the determination of arsenic directly as arsenious sulphide by weighing on a porcelain Gooch crucible is not practicable. The method was tried with various other minerals, and in but one case was the result within limits, due more to accident than to any virtues of the method. The difficulty seems to lie in the fact that the precipitate settles very compactly in the crucible, and prevents the carbon disulphide from obtaining more than a surface contact with it. In some instances the crucible was placed in a beaker, covered with carbon disulphide, and allowed to stand for twenty-four hours without any appreciable difference becoming manifest in the result.

Metallic Arsenic (*As*).—In the oxidation of the metallic arsenic a difficulty was encountered which the previous minerals had been free from. It was noticed that if the

conditions previously mentioned were followed, viz., that the caustic potash be brought to a state of fusion, and the powdered mineral added, a volatilisation of some of the arsenic invariably occurred. In fact, so rapidly did this take place that barely did the mineral come in contact with the fused potash but what the garlicky odour of arsenic was perceptible. To obviate this loss the following method was found to be the best, and, in fact, the only one that would give accurate results. The caustic potash was introduced into the crucible, carefully heated to drive out all moisture, and eventually brought to complete fusion. The flame was now removed, and the mass allowed to cool until it was almost solid, when the powdered arsenic was carefully spread over the surface of the potash. The platinum wire is now placed in position and the current closed. Should the potash have cooled to such an extent that the current will no longer pass through the mass, or at least only with difficulty, a very small flame carefully played under the crucible will remedy the trouble. The arsenic, if these directions are complied with, becomes gradually oxidised, and no volatilisation is perceptible. After the first ten minutes the crucible may be gently heated until its contents are again in a condition of fusion, and should be kept in such a state until the end of the oxidation. The current used for the operation registered 1 ampère in the Kohlrausch ampèremeter, when the potash was completely fused. At the beginning of the oxidation the resistance offered by the almost solid caustic potash is so great that the current barely registers, but this is exactly the condition that is desirable for thorough results. The current was allowed to run for thirty minutes, being reversed for the last five minutes. The results are as follows :—

0·0974 grm. of arsenic gave 0·1813 grm. of magnesium pyroarseniate = 90·11 per cent arsenic.

0·1052 grm. of arsenic gave 0·1961 grm. of magnesium pyroarseniate = 90·23 per cent arsenic.

The very slight residues which remained after the fusions were treated with water showed no signs of arsenic. The filtrates from the precipitations with magnesia solution were acidulated with hydrochloric acid and hydrogen sulphide added, to see if possibly some of the arsenic might be present as arsenious acid. No trace of the latter, however, was found.

Another sample of the powdered metal was dissolved in nitric acid, and the arsenic determined in the manner already indicated for the previously mentioned minerals, as magnesium pyroarseniate. It yielded 90·14 per cent arsenic.

In the two determinations of arsenic in the metallic arsenic, given above, the magnesium pyroarseniate was weighed on porcelain Gooch crucibles.

Rammelsbergite ($Ni.Co.Fe.)As_2$.—With this mineral more difficulty was encountered than with any other, and the results that are given below were obtained only after *seventeen* attempts at decomposition proved unsuccessful. The method used at first was the one which showed itself to be efficient for the decomposition of metallic arsenic, viz., 25—30 grms. of caustic potash and a current of 1 ampère running for thirty minutes, with five minutes reversal at the end of the oxidation. This proved an utter failure, as the residues from the fusion showed in all cases the presence of arsenic, while the results obtained varied from 53—67 per cent of arsenic. A former experience having shown that the non-oxidation might probably be due to the enclosure of particles of mineral on the platinum wire, a more frequent reversal of the current was tried. Using the same amount of caustic potash, and increasing the current strength from 1—1½ ampères, the current was reversed after the first ten minutes, and allowed to run in the opposite direction for three minutes. It was then passed up through the crucible again for five minutes, then again down through the platinum wire for three minutes, the process being continued for thirty minutes. The results were altogether unsatisfactory, large quantities of arsenic being found in the residues.

The amount of caustic potash was now increased from 25—30 grms. to 40 grms., the nickel crucible used being 1½ inches high and 2 inches wide. In six decompositions made under these conditions, the current in the first two had a strength of 1 ampère, in the second two of 1½ ampères, and in the last two it was increased to 1¾ ampères, the current being reversed in a manner similar to the one previously tried. The results in all cases were of a negative order, as arsenic was found in all the residues. An increase of the time limit was now tried with satisfactory results. Using 40 grms. of caustic potash the current was allowed to act for forty-five minutes. After various attempts to ascertain the best current strength for the purpose, it was found that a current that registers an ampère was the most satisfactory, and it should not be allowed to rise above this point, otherwise the decompositions are apt to be incomplete. In the oxidations given below, the current was reversed at the end of every ten minutes, for three minutes. Another phase of the operation that seems to be essential is to have the mineral in as fine a condition as possible. Using the conditions just given the residues from the fusions showed no arsenic, though they were most carefully examined by the wet method and also before the blowpipe. The arsenic was precipitated as magnesium ammonium arseniate and weighed as magnesium pyroarseniate in a platinum crucible, the filter being ignited separately after moistening with ammonium nitrate.

The results found were as follows :—0·1829 grm. of rammelsbergite gave 0·2598 grm. of magnesium pyroarseniate = 68·76 per cent arsenic ; 0·2168 grm. of rammelsbergite gave 0·3118 grm. of magnesium pyroarseniate = 69·62 per cent arsenic.

Another sample of the mineral dissolved in nitric acid and determined as magnesium pyroarseniate gave 70·34 per cent arsenic.

Chloanthite ($Ni.Co.Fe.)As_2$. — The mineral used for decomposition was a portion of the sample from Franklin, N.J., which was reported along with other minerals by Dr. Koenig in the *Proceedings* of the Academy of Natural Sciences of Philadelphia, 1889, 184. The decompositions were made contemporaneously with those of rammelsbergite, and for this reason many of the unsuccessful steps which were made with the latter mineral were also made with the chloanthite. The first oxidations were made with a current of one ampère, using 25—30 grms. of caustic potash and allowing the current to run for thirty minutes. As with the rammelsbergite, so here, too, only diverse results were obtained. Reversing the current every five minutes, after the first ten minutes, brought about a similar condition of affairs. The results were from 5 to 6 per cent low. The addition of copper oxide, as recommended by Dr. Smith in the oxidation of pyrites (*Journal of the Franklin Institute*, proceedings of the Chemical Section, vol. ii., p. 62), was now tried. The quantity of caustic potash used being increased at the same time with one sample of the chloanthite, an equal amount of copper oxide was mixed, and with another sample double the quantity of copper oxide. The other conditions were a current of 1½ ampères, a time limit of thirty minutes, with reversals of the current after the first fifteen minutes, and 40 grms. of caustic potash. This combination of conditions gave no better results than the previous one. Satisfactory results were eventually obtained under the following conditions, the copper oxide being dispensed with entirely : — The current was not allowed to register above 1 ampère, and the best results will be obtained if it is kept slightly below this mark. Thirty minutes was found to answer for complete decomposition, but for the sake of certainty it is advisable to allow the current to run for forty-five minutes, reversing it during the last five minutes. The amount of caustic potash used was 40 grms. The results obtained were as follows :—0·2332 grm. of chloanthite was decomposed as above. The fusion was treated with hot water and filtered. The filtrate was acidulated with hydrochloric

acid and warmed to expel the carbon dioxide present. On cooling, the arsenic was reduced with sulphurous acid, and after the expulsion of the excess of sulphurous acid, was precipitated with hydrogen sulphide in the cold. The precipitate of arsenious sulphide was filtered in a Gooch crucible after the solution had stood until it barely had the odour of hydrogen sulphide, and washed with cold water. The crucible and its contents were then placed in a beaker, carbon disulphide added, and allowed to stand twenty-four hours. The crucible was then removed from the beaker, its contents washed with alcohol, then with cold water, and finally dried for six hours at 105° C.; 0·2710 grm. of arsenious sulphide was found = 70·84 per cent arsenic; 0·2899 grm. of chloanthite treated in the same manner as the preceding gave 0·3325 grm. of arsenious sulphide = 69·93 per cent arsenic.

In the sample of the mineral analysed by Dr. Koenig and reported by him he found 70·66 per cent arsenic.

As will be seen from the above, accurate results were obtained by weighing the arsenic as arsenious sulphide. They are, however, but two out of a large number of determinations that were made in porcelain Gooch crucibles, and the only two which gave results sufficiently close to be utilised. The amount of sulphur precipitated with the arsenious sulphide must have been very small, otherwise the results, owing to the inefficacy of the carbon disulphide, would assuredly have been high. For this reason the author cannot recommend the method for general use.

The residues from the fusions were carefully examined for arsenic, but none was found to be present.

Smaltite (*Co.Ni.Fe.*) As_2.—From the experience gained with rammelsbergite and chloanthite, it was found very easy to oxidise the smaltite. The mineral used for the purpose was mixed with gangue, and therefore was first broken up, and the smaltite picked out as carefully as possible by hand. The resultant material, as shown by the analyses, still contained impurities. The conditions for oxidation are as follows:—A current of 1 ampère with the restrictions imposed under chloanthite, a time limit of forty-five minutes, and 40 grms. of caustic potash. Using those conditions the oxidation is complete, the residues showing not the least trace of arsenic. The results obtained were as follows:—

0·2233 grm. of smaltite gave 0·2813 grm. of magnesium pyroarseniate = 60·98 per cent arsenic.

0·1790 grm. of smaltite yielded 0·2199 grm. of magnesium pyroarseniate equalling 59·47 per cent arsenic.

The method of procedure resembled one already given. The fusion was acidified with hydrochloric acid, then made alkaline with ammonium hydrate, and the arsenic precipitated with magnesia solution, being finally weighed in a platinum crucible. In the latter of the two determinations, the garlic odour of arsenic was noticeable on igniting the filter paper, although it had previously been thoroughly saturated with a concentrated ammonium nitrate solution. This accounts for the slightly low result obtained, but it was not thought necessary to repeat the operation, since the residue showed that the oxidation was complete.

0·3136 grm. of the ore, dissolved in nitric acid, and the arsenic determined as magnesium pyroarseniate, in a platinum crucible, gave 0·3929 grm. of magnesium pyroarseniate, equals 60·65 per cent arsenic. The difference in percentage from the theoretical amount is due to the impurities in the mineral.

A study of the composition of rammelsbergite, chloanthite, and smaltite will show several points of interest. It will be seen from their formulæ that they each contain two atoms of arsenic to the molecule, while niccolite, cobaltite, arsenopyrite, &c., either have one atom of arsenic to the molecule, or have one atom of arsenic replaced by sulphur. Returning to the study of the conditions necessary for oxidation, it will be remembered that the amounts of caustic potash necessary, and the extents of time, were larger for the first three minerals than for any of the others, while the oxidations seem to proceed with greater difficulty. A cause for this that might be advanced, is that the oxides of the metals are united with greater tenacity to two arsenic atoms than they are to one, and require a greater expenditure of force for their separation. A somewhat similar occurrence was noticed by Dr. Smith in the oxidation of the metallic sulphides. Pyrrhotite, whose formula is in all probability either $Fe_{11}S_{12}$ or FeS, is decomposed with great readiness, while pyrite, which contains two atoms of sulphur to the molecule, succumbed only after repeated and many fruitless trials. What might be considered a curious feature in the oxidation of these arsenides is the fact that those containing two atoms of arsenic to the molecule are decomposed more readily by weak currents than they are by strong ones, while with the arsenides containing but one atom to the molecule, either strong or weak currents are equally efficacious. The only explanation that there is to offer for this seeming anomaly, is the one already gived, viz., the enclosure of particles of metal on the platinum wire. In those arsenides containing but one atom of arsenic to the molecule, the decomposition is in all probability so rapid that any enclosure of the mineral on the wire is practically impossible. In minerals like rammelsbergite and chloanthite we may assume that the decomposition proceeds by much slower stages, so that if the current is sufficiently strong to deposit metal on the cathode there is constantly present sufficient undecomposed mineral to be enclosed in the deposited metal.

Cobaltite (—(*Co.Fe.*)*As.S*).—This mineral was decomposed with great ease,—a result to be expected if we trace the similarity in composition between it and such minerals as gersdorfite, niccolite, &c. The conditions for oxidation are very similar to those of gersdorfite, with the difference that while, in the latter, the current was allowed to run only for twenty minutes, in the decomposition of cobaltite it ran for thirty minutes, with a five minutes reversal at the end. Otherwise the conditions for oxidation and for the subsequent decomposition of the fusion and the estimation of the arsenic, are the same as for gersdorfite. The magnesium pyroarseniate was weighed in platinum Gooch crucibles, the method being very accurate, owing to the fact there is no possibility for any volatilisation of the arsenic, and more rapid than weighing in a porcelain Gooch crucible, since the platinum crucible attains a constant temperature in a very short period of time. The results obtained were as follows:—

0·1032 grm. of cobaltite yielded 0·1006 grm. of magnesium pyroarseniate = 47·2 per cent arsenic.

0·1326 grm. of cobaltite yielded 0·1313 grm. of magnesium pyroarseniate = 47·93 per cent arsenic.

0·2250 grm. of the same ore was dissolved in nitric acid, the acid evaporated, the solution made alkaline with ammonium hydrate, and the arsenic precipitated with magnesia solution. The resultant magnesium ammonium arseniate was ignited in a porcelain Gooch crucible and gave 0·2229 grm. of magnesium pyroarseniate = 47·96 per cent arsenic.

(To be continued.)

Society of Arts.—In consequence of the illness of Prof. W. C. Unwin, F.R.S., the Howard Lectures on "The Development and Transmission of Power from Central Stations," which he was announced to deliver on February 5th and five following Friday evenings, has been postponed.

The Determination of Creatinine in Urine.—J. Moitessier.—Nothing can be effected by methods for determining creatinine founded upon its direct precipitation from urine, in the state of a double zinc-creatinine chloride. Neubauer's method, though tedious and delicate, is exact, and is the only one which can be safely used.—*Bull. Soc. Chim. de Paris.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

December 17th, 1891.

Dr. W. H. Perkin, F.R.S., in the Chair.

(Concluded from p. 48).

85. "*The Sulphochlorides of the Isomeric Dibromonaphthalenes.* (I.)." By Henry E. Armstrong and E. C. Rossiter.

Many statements are on record with reference to the dibromonaphthalenes which are difficult to reconcile; the preparation of characteristic derivatives which could be made use of in distinguishing the various modifications is therefore of importance, and the more they are studied the more is this found to be the case; indeed, more than usual difficulty attends their investigation, as little or no reliance can be placed either on appearance or melting-point, a slight impurity sufficing to produce most misleading changes in these; moreover, the separation of isomerides is made very difficult by their tendency to crystallise together, forming mixtures which simulate pure substances in a most remarkable manner. Unfortunately, also, at the high temperatures requisite to effect the hydrolysis of many of their sulphonic acids, slight decomposition takes place, in consequence of which an impure product is obtained.

Eight of the ten possible dibromonaphthalenes have been prepared, only the 1 : 1'-$\alpha\alpha$- and the 2 : 3-$\beta\beta$-modifications being unknown. Five of the modifications are referred to in the present notice, viz.:—

1 : 4-Dibromonaphthalene, prepared by brominating naphthalene.

1 : 4'-Dibromonaphthalene, prepared from Guareschi's bromonitronaphthalene by reducing, diazotising, &c.

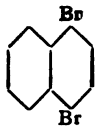
1 : 3-Dibromonaphthalene, prepared by Meldola's method.

1 : 2'-Dibromonaphthalene, prepared by brominating β-bromonaphthalene.

1 : 3'-Dibromonaphthalene, prepared by the action of PBr_5 on the bromosulpho-acid obtained from the Dahl modification of β-naphthylaminesulphonic acid.

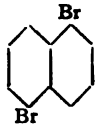
These dibromonaphthalenes are readily sulphonated by heating with twice their weight of H_2SO_4 (so-called 100 per cent acid) on the water-bath until dissolution is complete; on adding potassium carbonate in slight excess to the moderately dilute solution of the sulpho-acid, the potassium sulphonate separates almost entirely from the liquid, and, after re-crystallisation, is converted into sulphochloride.

The properties of the sulphochlorides are summarised in the following table:—



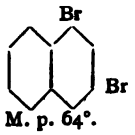
M. p. 82—83°.

Yields only one sulphonic acid.
SO_2Cl, prismatic needles; m. p. 120°.



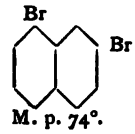
M. p. 130°.

Yields only one sulphonic acid.
SO_2Cl, prismatic needles; m. p. 175°.



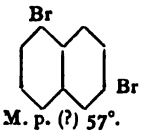
M. p. 64°.

Yields two sulphonic acids.
α-SO_2Cl, prisms or highly refractive stumpy crystals; m. p. 157°.
β-SO_2Cl, prismatic needles or long flexible plates; m. p. 128°.



M. p. 74°.

Only one sulphonic acid isolated as yet.
SO_2Cl, prismatic needles which, like the corresponding dichloro-derivative, become opaque on keeping; m. p. 113°.



M. p. (?) 57°.

Only one sulphonic acid isolated as yet.
SO_2Cl, massive prisms; m. p. 145°.

It was stated by Armstrong and Wynne, in 1886 (these *Proceedings*, p. 233), that when 1 : 3'-naphthalenedisulphonic acid is treated with bromine, it affords a dibromo-β-monosulphonic acid isomeric with that prepared by Jolin from naphthalene-β-sulphonic acid; this conclusion was based on the production from the acid by hydrolysis of a dibromonaphthalene of much lower melting-point than the 1 : 4-modification, and altogether different from it in appearance: it is now found that the product of hydrolysis in question was impure 1 : 4-dibromonaphthalene, and it follows, therefore, that the acid from which it was derived is identical with Jolin's.

It is to be noted that whereas the dibromonaphthalenes all have higher melting-points than the corresponding dichloronaphthalenes, no such relation obtains between the sulphochlorides of corresponding dichloro- and dibromonaphthalene.

86. "*The Action of Alcohols on Sulphonic Chlorides as a Means of Producing Ethereal Salts of Sulphonic Acids.*" By Henry E. Armstrong and E. C. Rossiter.

It is customary to prepare ethereal salts of sulphonic acids by the interaction of the silver salt and the bromide or iodide of a carbonyl radicle. The authors find that several, but by no means all, of the dibromonaphthalene-sulphochlorides may be converted into the ethereal salt by boiling with ordinary dehydrated alcohol; the 1 : 4-sulphochloride especially is remarkable for the readiness and completeness with which it undergoes this change, but a small proportion being hydrolysed and converted into sulphonic acid. The 1 : 4'-sulphochloride under similar conditions is entirely hydrolysed; its behaviour thus affords a striking contrast to that of the 1 : 4-compound, especially as both are β-sulphonic derivatives. The 1 : 2'-sulphochloride, which is an α-sulphonic derivative, also yields ethereal salts when boiled with alcohols, although in relatively small amount; this is a further proof that the formation of ethereal salts is not a function of the β-sulphonic radicle.

The peculiar behaviour of the 1 : 4-sulphochloride is of interest in connection with Heller's observation (these *Proceedings*, 1889, 121) that 1 : 4-dibromo-, dichloro-, and chlorobromo-naphthalenes behave in a peculiar manner on treatment with SO_3HCl, being converted into sulphones, whereas isomeric compounds yield sulphonic acids as chief product.

It is proposed to study the behaviour of a number of typical sulphochlorides towards alcohols and sodium derivatives of alcohols.

*87. "*The Action of Bromine on α- and β-bromonaphthalene.*" By Henry E. Armstrong and E. C. Rossiter.

It is well known that when naphthalene is submitted to the action of two molecular proportions of bromine, a product is obtained from which a considerable amount of 1 : 4-dibromonaphthalene may be separated without difficulty by crystallising from alcohol, leaving as major product a substance melting at 68—70°; numerous unsuccessful attempts have been made to determine the nature of this product, and although Magatti and also Guareschi have separated a small quantity of 1 : 4'-dibromonaphthalene from it, down to the present time its constitution has remained a mystery.

As β-dibromonaphthalene is formed in small quantity on brominating naphthalene, the action of bromine on this compound was first studied; it is found to afford 1 : 2'-dibromonaphthalene almost as sole product.

To determine the nature of the product of low melting-point from naphthalene and two molecular proportions of bromine, it was sulphonated, and attempts were made to effect a separation by re-crystallising the potassium salt of the resulting acid; as these were unsuccessful, sulphochloride was prepared: by crystallising this from benzene and from acetic acid, a considerable fraction of the product was ultimately recognised as the sulphochloride of 1 : 4-dibromonaphthalene. The residual sulphochloride melted at 107—110°; numerous attempts were made to purify this by crystallisation without success; it was hydrolysed at 260—270°, but the product had a low melting-point and could not be identified; but on boiling it with alcohol a considerable amount of the ethylic salt of 1 : 4-dibromonaphthalenesulphonic acid was obtained. It was, therefore, evident that on brominating naphthalene much more 1 : 4-dibromonaphthalene is formed than is commonly supposed. Fresh attempts were then made to resolve the crude product melting at about 70° into its constituents by means of solvents. Eventually, on fractionally extracting it with light petroleum, it was found that the first separations from the last extracts melted at 115—125°, and on crystallising this product from alcohol, it melted at 129—130°, and was identified as 1 : 4'-dibromonaphthalene.

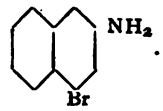
A small quantity of 1 : 4-dibromonaphthalene was obtained from the first extractions by petroleum; the rest of the product melted at 68—70°. On crystallising this latter from alcohol a further separation of 1 : 4-dibromonaphthalene was obtained, but the residue still melted at 68—70°. However, by alternately crystallising this last product from petroleum and alcohol, it was gradually split up into 1 : 4- and 1 : 4'-dibromonaphthalenes, the melting-point of the residue always remaining constant at 68—70°.

From these results it is concluded that the substance melting at 68—70° is a mixture of 1 : 4- and 1 : 4'-naphthalene, and from the weights obtained of these it is concluded that the 1 : 4-dibromonaphthalene constitutes about four-fifths and the 1 : 4'- one-fifth of the mixture.

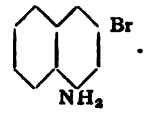
No 1 : 3-dibromonaphthalene was obtained. As a mixture of 1 : 4- and 1 : 3-dichloronaphthalenes is obtained by the action of chlorine on naphthalene, the production of the 1 : 4- and 1 : 4'-compounds by the action of bromine would seem to be an indication of a great difference between the action of chlorine and bromine on naphthalene; but such is not the case. The formation of the dichloronaphthalenes is preceded by that of a comparatively stable tetrachloride, but no such compound is produced by the action of bromine; probably a highly unstable dibromide is first formed, which is at once resolved into hydrogen bromide and bromonaphthalene, and the latter is then further acted on. Experiments, of which an account will be given later on, show that when chloronaphthalene is chlorinated results are obtained very similar to those obtained on brominating bromonaphthalene.

"88. "*The Action of Bromine on a Mixture of Ortho- and Paranitro-α-acenaphthalids.*" By HENRY E. ARMSTRONG and E. C. ROSSITER.

Meldola, in 1885 (*Trans.*, pp. 497—518), described two series of compounds derived, one from brominated α-acenaphthalide, the other from nitrated acenaphthalide; the former was converted by nitration into nitrobromacenaphthalide, from which the amido-group was eliminated, and the resulting nitrobromonaphthalene was reduced, a bromonaphthylamine being thus obtained, which, judging from previous observations, must necessarily be the compound of the formula—



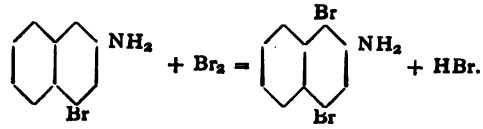
Nitrated acenaphthalide was known to be a mixture of the ortho- and para-derivatives; by brominating the mixture Meldola obtained a single product which he supposed to be derived from the *para*-constituent, and therefore he regarded the bromonaphthylamine obtained by eliminating the amido-group and then reducing as the isomeride of that prepared from bromacenaphthalide, viz., as—



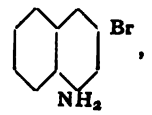
From the bromonaphthylamines from the two sources, Meldola prepared dibromonaphthylamines, from which he then prepared dibromonaphthalenes, obtaining in this way a modification melting at 74° from each source. Some time after the appearance of his paper (*cf.* these *Proceedings*, 1886, 172), he was led to modify his views of the constitution of the compounds he had obtained in consequence of the discovery by Stallard that the bromophthalic acid which Meldola prepared by oxidising one of his dibromonaphthylamines was derived from an α- and not from a β-bromonaphthalene; Meldola therefore suggested that the one amine was the compound $NH_2 : Br : Me = 2 : 4 : 1'$, and the other the compound $NH_2 : Br : Me = 1 : 3 : 3'$ or $1 : 3 : 2'$.

Wishing to prepare the 1 : 1'-dibromonaphthalene, the authors proceeded to repeat Meldola's work, as the argument which he made use of appeared to be a sound one, and there was, therefore, reason to think that the dibromonaphthalene which he had obtained starting from brominated acenaphthalide was the 1 : 1' modification; that obtained from the other source the authors were inclined to expect would prove to be the 1 : 2'-modification, which is known to melt at 74°.

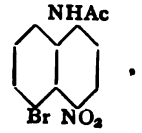
On preparing the two bromonaphthalenes in accordance with Meldola's directions, products were obtained, however, which both melted at 82—83°, the identity of which with 1 : 4-dibromonaphthalene was placed beyond doubt by conversion into the sulphochloride melting at 118° to 120° and the ethylic sulphonate melting at 156—157°. The production of 1 : 4-dibromonaphthalene from the bromonaphthylamine prepared from nitrated parabromacenaphthalide is easily understood, thus—



Its production from a bromonaphthylamine of the formula—



however, is clearly impossible; but it was conceivable that a heteronucleal derivative is formed on brominating paranitracenaphthalide, viz.:—



In this case the bromonaphthylamine obtained on eliminating the NHAc group and reducing should be convertible into 1 : 1'-dibromonaphthalene; according to Meldola it yields 1 : 3-dibromonaphthalene, but he was led to form this conclusion only by the appearance and melting-point of the product. The authors have prepared the dibromonaphthalene in question, and have proved it to be the 1 : 3-compound, as stated by Meldola, by converting it into the two sulphochlorides melting at 127° and 157° characteristic of this modification; and by completely reducing the bromonaphthylamine in question they have obtained β-naphthylamine.

There appears to be but one explanation possible of these results, viz., that when a mixture of ortho- and para-nitracenaphthalides is brominated, the ortho-compound —not the para-, as Meldola supposed—is alone attacked, and that consequently the same nitrobromonaphthalene is obtained on displacing the acetamido-group in nitrated parabromo-α-acenaphthalide, and in the product of the action of bromine on a mixture of the ortho- and para-nitro-derivatives of α-acenaphthalide.

Meldola, although struck with the remarkable similarity of the two series of compounds which he prepared, was led to notice certain differences: thus he obtained bromonaphthylamines melting, the one at 71·5°, the other at 62°; but the authors find that both products melt at 72°, and that the dibromonaphthylamines prepared from them melt at the same temperature, viz., 106°. Messrs. Miers and Pope have examined a number of the pairs of products, and report that corresponding compounds are not only identical in form, but also in optical properties, and as no case is on record of different substances being alike both morphologically and optically, there can be no doubt of the correctness of the explanation now advanced.

89. "*Camphrone, a Product of the Action of Dehydrating Agents on Camphor.*" By Henry E. Armstrong and F. S. Kipping.

The action of concentrated sulphuric acid on camphor appears to have been first examined by Chautard; it was subsequently studied by Fittig, Schwanert, and Kachler, all of whom agree in stating that under suitable conditions an oily product, having a strong peppermint odour, is formed, isomeric with acetophorone, $C_9H_{14}O$, which consequently has figured in chemical literature under the name *camphorone*. The various statements regarding the properties of this substance, however, are by no means confirmatory, Fittig stating that it boils at 204—205°, and that it has a relative density of 0·939 at 12°, whereas Schwanert gives 230—235° as its boiling-point and 0·9614 at 20° as the relative density.

Armstrong and Miller noticed the presence of a substance having properties simi ar to those of the product obtained by means of sulphuric acid among the products of the action of zinc chloride on camphor; but attempts which they made to isolate a definite substance from their crude product were unsuccessful.

It appeared probable that, with the aid of the improved methods of treating ketonic compounds now known, it would be possible to separate the characteristic constituent from the crude oil, and this has proved to be the case.

On treating the fraction boiling at 238—242° of the oil prepared by means either of sulphuric acid or of zinc chloride with phenylhydrazine, a mixture of a crystalline hydrazone with dark coloured oily products is obtained; the purified hydrazone crystallises in yellowish plates and melts at about 108°. By boiling it in alcoholic solution with ferric chloride and muriatic acid, an oil is obtained which yields a hydrazone identical with that from which it was prepared; on distilling this oil the thermometer rapidly rises to 245°, the greater part of the liquid passing over at 245—247°. On treatment with hydroxylamine the oil is converted into a hydroxime which crystallises in long prisms melting at 85—86°, of which the acetyl derivative melts at 69—70°.

The determination of the composition of these compounds presents considerable difficulty; analyses of the oil gave the following results:—

Carbon, per cent	80·84	80·88
Hydrogen, „	8·13	8·14

—numbers which agree satisfactorily with the formula $C_{10}H_{12}O$. But in numerous analyses of the hydroxime, the carbon was found to vary from 72·4—72·8 per cent; hydrogen from 7·8—8·0 per cent; and nitrogen from 8·6—8·9 per cent: these values do not agree with those required by a compound of the formula $C_{10}H_{12}N(OH)$, except the nitrogen values (C = 73·6, H = 7·27, N = 8·6). The acetyl derivative of the hydroxime gave similar results. The hydrazone was found to contain 12—12·2 per cent of nitrogen, the calculated value for—

$$C_{10}H_{12}N_2HPh$$

being 11·8. Evidently it is necessary to make a more complete study of the compound to place its composition beyond doubt, especially as the formula $C_{10}H_{12}O$ is a very remarkable one.

On oxidising the oil with nitric acid it yields an acid which crystallises well.

Obviously the substance is one of considerable interest, and its further investigation is likely to throw light on the still open question as to the structure of camphor. As the yield, even of the crude product, is small, and the preparation of the pure substance is a matter of considerable difficulty, it appears desirable to make this preliminary announcement, now that workers are becoming so numerous in this field.

90. "*Metaxylenesulphonic Acids (II.).*" By G. T. Moody, D.Sc.

In a previous communication (*Proceedings*, 1888, p. 77), the author has described the preparation of 1 : 2 : 3-metaxylenesulphonic acid, and has called attention to the fact that only the 1 : 3 : 4-acid is formed on direct sulphonation of the pure hydrocarbon. Attempts to prepare the symmetrical 1 : 3 : 5-sulphonic acid have not yet met with success, the sulphonation of 1 : 3 : 4-acetmetaxylid failing to give the required substitution.

Acetmetaxylid (1 : 3 : 4) is readily sulphonated when heated for some time at 140° with 1½ times its weight of 20 per cent anhydrosulphuric acid, and on boiling the solution after the addition of water, metaxylidinesulphonic acid ($Me_2 : NH_2 : SO_3H = 1 : 3 : 4 : 6$) is obtained. It crystallises from water, in which it is only very sparingly soluble, in well-formed, slender needles, insoluble in alcohol and other common solvents; it does not change at 290°, and when heated to a higher temperature, decomposes without having previously melted. The sodium salt, $C_6H_3Me_2NH_2SO_3Na,H_2O$, is exceedingly soluble in water and crystallises in flat plates.

On diazotising the acid and subsequently boiling the solid product with dehydrated methylated spirit, ethoxymetaxylenesulphonic acid ($Me_2 : OEt : SO_3H = 1 : 3 : 4 : 6$) was obtained. The sodium salt of the acid crystallises in long, slender needles, which effloresce when exposed to the air; the sulphochloride crystallises from light petroleum in beautiful orthorhombic plates, melting at 56°; the sulphonamide separates from dilute alcohol in small white scales, or flat needles which melt at 169—170°.

When the diazo-product is boiled with bromhydric acid, the corresponding bromoxylenesulphonic acid ($Me_2 : Br : SO_3H = 1 : 3 : 4 : 6$) is formed. It crystallises in long slender needles, and does not melt at 270°, but at a considerably higher temperature melts with decomposition. The sodium salt agrees with the description given by Weinberg (*Ber.*, xi., 1062), who obtained it on bromination of a dilute aqueous solution of barium 1 : 3 : 4-metaxylenesulphonate; but the sulphochloride obtained by the author, which crystallises in splendid oblique prisms, melts at 2° higher (62—63°), whilst the sulphonamide melts at 5° lower (189°) than found by

Weinberg. The melting-point of the sulphonamide agrees with that given by Sartig (*Annalen*, ccxxx., 335), who prepared it by sulphonating metaxylidine, and subsequently replacing amidogen by bromine. It thus appears that both xylidine and acetxylid give the same acid on sulphonation, and that the displacement of hydrogen in the amido-group by acetyl does not lead to any change in the position taken up by the sulphonic group.

"91. "*The Action of Propylene Bromide on the Sodium Derivatives of Ethylic Acetoacetate and Ethylic Benzoylacetate.*" By W. H. PERKIN, Jun., Ph.D., F.R.S., and JAMES STENHOUSE.

The product from ethylic acetate is a mixture of ethylic acetylmethyltrimethylenecarboxylate and ethylic methyldiacetyladipate. The former is found to yield a well-crystallised hydroxime (m.p. 153—155°); when boiled with water, it is gradually converted into acetoisobutyl alcohol. Ethylic methyldiacetyladipate is decomposed on distillation into an oil which is a mixture of at least two compounds, as, when hydrolised, it yields dimethyldihydropentenedicarboxylic acid, together with dimethyldihydropentene methyl ketone.

Ethylic benzoylmethyltrimethylenecarboxylate and several of its derivatives are also described in the paper.

92. "*Derivatives of Tetramethylene.* By W. H. PERKIN, Jun., Ph.D., F.R.S., and W. SINCLAIR, B.Sc.

By the action of bromine in presence of phosphorous on tetramethylenecarboxylic acid, the authors have obtained an almost quantitative yield of the monobromo-derivative. They describe its methylic salt, and the corresponding hydroxy-, acetoxy- and ethoxy-acids. By acting on the chloride of the acid with zinc methyl and ethyl, they have prepared tetramethylene methyl and ethyl ketones, of which they also describe the reduction products.

CORRESPONDENCE.

EXPLOSION OF A SODIUM BOTTLE.

To the Editor of the Chemical News.

SIR,—A short time since we had a violent explosion in our laboratory. On investigation it proved to arise from the explosion of a bottle containing about 2 lbs. sodium, which had been as usual preserved in naphtha; it had not been touched for about two years, and possibly the naphtha had evaporated. Can any of your correspondents state the cause of the violent explosion which occurred, scattering the bottle and its contents all over the room? If it had occurred at night it would have been very dangerous; as it was it occurred in the day at a time when no one was present, much of the sodium had ignited. Is there this danger in storing sodium?—I am, &c.,

A. MERRY.

Hafod Isha Works, Swansea.
Jan. 23, 1892.

MELTING SNOW IN THE STREETS.

To the Editor of the Chemical News.

SIR,—There has been this winter the usual crop of inventors who, without the slightest knowledge of the subject they advocate, endeavour to enlist the time and money of others as ignorant as themselves in a very foolish scheme, *i.e.*, to use ordinary gas to melt the snow which obstructs the streets, some of the sanguine having gone to some expense in demonstrating what was already known, *i.e.*, the possibility of it irrespective of cost.

How absurd such a project is can be easily seen by comparing the known heating value of coal-gas with the work to be done.

Six inches deep of average snow, when melted, becomes half an inch depth of water, 24 square feet of which will weigh 62½ lbs., or 23·4 lbs. per square yard. At this rate the snow on one mile (or 1760 yards) of a street 20 yards wide would, if 6 inches deep, weigh 823,680 lbs., or 363½ tons.

The heating power of London gas is 660 units per cubic foot, *i.e.*, one cubic foot of coal-gas will heat 660 lbs. of water 1° F., and of this we may take it as a maximum that 500 units could be utilised.

It has been proved repeatedly and beyond question that 1 lb. of snow at freezing-point requires 150 units of heat to melt it and raise the temperature of the water obtained to 40° F., and this effect would be produced on 3½ lbs. of snow by the consumption of one cubic foot of coal-gas. From the above data it will be found that to melt the snow in the assumed mile of street would require the consumption of 247,000 cubic feet of gas, costing, at 3s. per 1000 cubic feet, a little over £37, or at the rate of £3256 per square mile.

As there are a great many square miles of streets in many towns, and as the snowfall has already been nearly double that assumed, it will be seen that the problem is most certainly not one to be solved by this method. Even if we were to assume that the cost of gas and labour was not prohibitive, the fact that the ground itself is usually colder than 32° must be considered, and the ground would also have to be warmed, or a thin surface of glassy ice, of the most slippery and dangerous kind, would remain after the snow was removed; this alone would condemn the project as being unworthy of consideration.—I am, &c.,

THOMAS FLETCHER, F.C.S.

Warrington.

DISCUSSION AT THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—At the meetings of the London Section of the Society of Chemical Industry, and also, I believe, at those of the Society of Public Analysts, a shorthand writer is employed to report the discussions which take place after the reading of papers. I venture to suggest that the same course be adopted at the meetings of the Chemical Society.

Under the present arrangements, whatever they may be, the reporting can only be described as sketchy. If a discussion is to be printed at all it should surely be printed as it takes place, with the exception of such *lapsus linguæ* as *will* occur at the Chemical Society and, I suppose, elsewhere.

Moreover, is not a shorthand reporter almost as good a deterrent as it is possible for a president to be?

These remarks are called forth by a perusal of the report of the meeting of December 17th, as printed in your issue of January 22nd.—I am, &c.,

ONE WHO LISTENED.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 2, January 11, 1892.

The Spontaneous Oxidation of Humic Acid and of Vegetable Mould.—MM. Berthelot and G. André.—Humic acid, on exposure to light, turns yellow and evolves carbonic acid. No trace of nitric acid has been detected. The same reaction was observed on treating vegetable mould with a cold dilute solution of potassa.

There is then passed into the filtrate a current of carbonic acid to remove the barium hydroxide until the alkaline reaction has disappeared. It is then boiled for half an hour to expel free carbonic acid, filtered whilst hot, and washed with hot water. The second filtrate, which contains merely barium nitrate, is largely diluted, and dilute sulphuric acid is added. From the weight of the barium sulphate precipitated the nitric acid present may be readily calculated.

If, in the substance containing the nitric acid, there is present beside mercury and arsenic—or nitric acid—an alkaline metal, the quantity of nitric acid present can be determined by this method only if the alkali present does not suffice to convert all the nitric acid into nitrate of alkali, and if the quantity of the alkali itself is already known. Only that part of the nitric acid is taken up by the baryta which the alkali does not suffice to combine with. The nitric acid united with the alkali cannot be determined but merely calculated.

4. For determining chlorine in presence of mercury and arsenic acid, or phosphoric acid, the solid substance is boiled for fifteen minutes with an excess of solution of baryta and filtered. The precipitate, after washing, contains no chlorine, and the filtrate no mercury. In the filtrate the chlorine is determined after acidulation with nitric acid in the usual manner as silver chloride.

5. For determining sodium in presence of mercury and phosphoric acid, the hydrochloric or nitric solution of the substance is mixed with baryta water until the reaction is slightly alkaline and then boiled for fifteen minutes. It is then filtered and washed until free from baryta. In the precipitate are found the mercury and the phosphoric acid, whilst the solution contains all the sodium, barium hydroxide, and barium salts.

After the baryta has been precipitated with sulphuric acid in the boiling solution previously acidified, and after the precipitate has been filtered off, the filtrate is first concentrated in a platinum capsule and then evaporated completely to dryness in a tared crucible. From the weight of the ignited residue, which consists of sodium sulphate, the proportion of sodium in the substance is known.

6. The determination of sodium along with mercury and arsenic acid is effected by heating the substance gently in a tared porcelain crucible along with solid ammonium chloride, until the weight is constant. The residue is taken as sodium chloride.

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.

By CH. MALOT.

The phosphoric acid is first separated in the well-known manner as ammonium phosphomolybdate, the precipitate is dissolved in ammonia, and re-precipitated with magnesia mixture. After filtration the ammonium-magnesium phosphate is dissolved upon the filter in nitric acid of specific gravity 1·2, and the phosphoric acid is determined volumetrically with a solution of uranic nitrate. In this titration the author evades the spotting test with potassium ferrocyanide for detecting the end of the reaction by making use of tincture of cochineal, and of the property of uranium oxide to form a green lake with the colouring matter of cochineal. The nitric solution is mixed with a few drops of tincture of cochineal (obtained by treating cochineal with boiling water), an excess of the tincture being avoided, as a too intense colour interferes with the sensitiveness of the reaction. Ammonia is then added to the solution until a permanent violet colour is produced, and this colour is again removed by the addition of a drop or two drops of nitric acid.

He adds further 5 c.c. of a solution of sodium acetate (containing per litre 100 grms. of the salt), and then 50 c.c. of glacial acetic acid, heats to 100°, and titrates the hot solution with a neutralised solution of uranium nitrate of known efficacy. Each drop of this solution produces in the liquid mixed with cochineal tincture a greenish-blue spot the further the precipitation has advanced. It disappears on shaking, and the rose colour of the cochineal re-appears until the precipitation is complete.

As soon as all the phosphoric acid has been precipitated by the solution of uranium nitrate, the liquid takes a bluish-green colour, which is not affected by any further addition of uranium nitrate. If a drop of the solution is brought in contact with a particle of ferrocyanide there ensues no colouration; in order to produce a distinct brown colour a little more of the uranium nitrate solution must be added.

It is convenient to use a solution of uranium, of which 1 c.c. corresponds to 2 m.grms. phosphoric acid, and standardised to a solution of phosphoric acid of known strength, carefully observing the above conditions and heating the solution to 100°.

The results obtained by Malot, according to this method, always agree to $\frac{1}{10}$ c.c. or $\frac{1}{5}$ m.grm. phosphoric acid. As the method, in addition to its accuracy, is very expeditious, the author prefers it both to the "spotting" test with ferrocyanide and to the direct weighing of the magnesium pyrophosphate.—*Zeit. Anal. Chemie.*

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending December 31st, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To General A. De Courcy Scott, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, January 9th, 1892.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 166 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 166 samples examined, 160 were found to be clear, bright, and efficiently filtered. Four were recorded as "slightly turbid" (S.T.), and two as "very slightly turbid" (V.S.T.).

Although the generally turbid and flooded condition of the rivers throughout November was appreciably exceeded during the following month by reason of the heavy rainfall, the state of the December water supply showed upon the whole a distinct improvement. Thus, taking the Thames-derived supply for comparison, the mean degree of colour-tint was found to be reduced from 22·1 : 20 to 18·7 : 20; the mean amount of oxygen expended in oxidation from 0·101 grain per gallon to 0·079 grain; the mean

amount of organic carbon from 0·250 to 0·240 part in 100,000 parts; and the maximum amount of organic carbon in any single sample examined from 0·391 part to 0·319 part. Similarly, in the case of the New River and East London Companies' supplies for the two months respectively, the results obtained during December showed a similar improvement over those recorded in our previous month's report.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

ON A

RAPID METHOD FOR THE ACCURATE RECOGNITION OF SULPHIDES, ARSENIDES, ANTIMONIDES, AND DOUBLE COMPOUNDS OF THESE BODIES WITH METALS.*

By CHARLES A. BURGHARDT, Ph.D., &c.

(Concluded from p. 44).

Antimony Sulphide.

Stibnite, Sb_2S_3.—Fused in the same kind of apparatus as that used for the sulphides of arsenic, yielded sulphuric acid in the water and a mixture of Sb_2O_3 and Sb_2O_5. A little sulphuric acid was also detected in the water which had been used to boil the residue in the fusion tube. On adding a solution of potassium bisulphate to the residue in the fusion tube, and a piece of pure metallic zinc, antimoniuretted hydrogen was at once evolved, and a mirror of metallic antimony obtained on heating the delivery tube to redness. Other tests applied proved this mirror to be really antimony. The mineral did not give reactions for any other element likely to be present, hence it was sulphide of antimony.

If it is suspected that both arsenic and antimony are present in a mineral in large amount, they can be easily separated from each other by substituting sodium nitrate for ammonium nitrate, when a compound of antimony and sodium, insoluble in cold water, is obtained (antimoniate of sodium), whilst the arsenic forms arsenite and arsenate of sodium, both of which are soluble in cold water after standing some time.

Löllingite.

$FeAs_2$—Fused with ammonium nitrate in a platinum crucible or porcelain crucible. Melt, red coloured. Dissolved in hot water gave the reactions for arsenious and arsenic acid with silver nitrate and the usual arsenic reactions. The insoluble residue gave the reactions for iron. The mineral was therefore an arsenide of iron.

Proustite.

Ag_3AsS_3.—Fused in the same manner as the last-mentioned mineral, yielded a black residue containing arsenic oxide (this residue will be the subject of special examination, as it is peculiar). The melt was treated to separate the black residue. A solution of silver sulphate was obtained, which gave the characteristic reactions for silver and sulphuric acid. The black residue was treated with the acid potassium sulphate solution and metallic zinc, and arsenic was detected in the usual manner. The solution in water also gave the characteristic reaction for arsenic acid with silver nitrate. All the silver of the proustite was converted into sulphate, on account of the high percentage of sulphur in this mineral. The mineral was therefore a sulph-arsenite of silver.

Pyrargyrite.

Ag_3SbS_3.—Treated in the same way as the preceding mineral, sulphate of silver was obtained in solution in water, and insoluble antimonious and antimonic oxide (Sb_2O_3 and Sb_2O_5) remained as a residue. The antimony reactions were obtained, and only silver and sulphuric acid detected; consequently, the mineral was a silver sulph antimonite.

Argentite.

Ag_2S.—On treating this mineral in the same manner as pyrargyrite, sulphate of silver was produced in small amount, owing to the small percentage of sulphur present in argentite. On adding a small quantity of "flowers of sulphur" to the powdered mineral, and then fusing the mixture with the ammonium nitrate, a larger quantity of silver sulphate was obtained. The solution gave the reactions for silver and sulphuric acid only; consequently, the mineral was a sulphide of silver.

Iron Pyrites.

Marcasite. Pyrites. FeS_2.—Fused as above, gave a reddish brown residue of ferric oxide, Fe_2O_3, and a brown solution in water, which gave the characteristic reaction for ferric salts with potassium ferrocyanide solution, and also the reaction for sulphuric acid. The mineral was therefore sulphide of iron.

Galena.

PbS.—Gave a white residue (insoluble in water) of lead sulphate, and nothing in solution. The residue was dissolved in hot hydrochloric acid; when a portion of the solution gave a white precipitate (of barium sulphate) on the addition of a solution of barium nitrate, and another portion of the hydrochloric acid solution, on being neutralised with sodium carbonate and boiled with a solution of potassium bichromate, gave the characteristic yellow lead chromate reaction. The white lead sulphate residue mentioned above, on being treated *directly* with the solution of potassium bichromate, also gave the lead chromate reaction. The mineral was therefore a sulphide of lead.

Copper-glance (Redruthite).

Cu_2S.—Gave a blue melt whilst hot, which became brown on cooling. The melt dissolved completely in water into a blue solution, which gave the usual reactions for copper and sulphuric acid. The mineral was therefore a sulphide of copper.

Bismuth-glance.

Bi_2S_3.—The melt was brown when cold. A solution of sulphate of bismuth was obtained, which gave the reactions for bismuth and sulphuric acid. An excellent and delicate reaction for bismuth is that which was shown to me by Professor Bunsen, at Heidelburg, twenty-one years ago, which I have never yet seen described in any work on qualitative analysis. In applying it to the solution of the melt first add a slight excess of caustic soda solution to it, when a white precipitate of hydrated bismuthic oxide ($Bi_2O_3H_2O$) is obtained. In another vessel add an excess of caustic soda solution to a solution of stannous chloride, when a white precipitate of hydrated stannous oxide ($SnOH_2O$) falls out, but immediately re-dissolves in the excess of caustic soda. The bismuth precipitate obtained as above is washed into a white basin and a portion of the caustic stannous solution poured upon it and well stirred with it, when very soon a dense black precipitate is seen in the white basin, this precipitate being an oxide of bismuth, Bi_2O_2, formed by the reduction of the Bi_2O_3 through the SnO.

Millerite.

NiS with Co and Fe.—Gave a green solution of sulphate of nickel, which gave the characteristic reactions for nickel and sulphuric acid, and also those for cobalt and iron. There was an insoluble brown residue of ferric oxide from the melt. The mineral therefore was a sulphide of nickel.

* From the *Mineralogical Magazine*, Vol. ix., No. 43.

WEGELIN AND HÜBNER, Halle-on-Saale.

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CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE

Edited by Wm. Crookes, F.R.S. (WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE") *Established Forty-Eight Years.*

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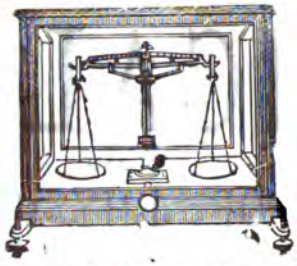

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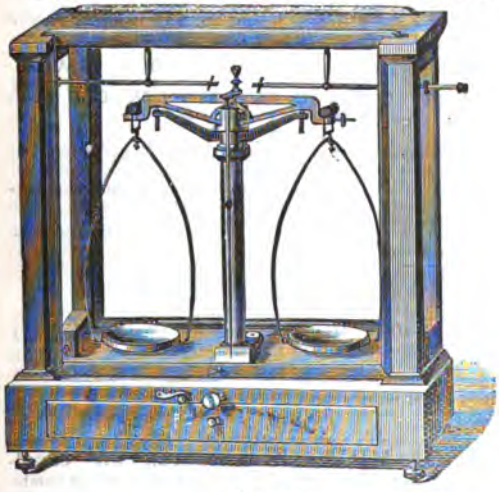

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1680.

AGRICULTURAL CHEMISTRY.

The Action of Electric Currents upon the Growth of Seeds and Plants.

By Dr. JAMES LEICESTER,
Lecturer on Chemistry at the Merchant Venturers' Technical School, Bristol.

A.—Zinc plate buried in the soil and about 1 square foot in size.

B.—Plate of copper having the same dimensions as the zinc plate, and connected at the top by a copper wire above the surface (c) with the copper plate (B).

D.—A box about 3 feet long and about 2½ feet wide filled with soil.

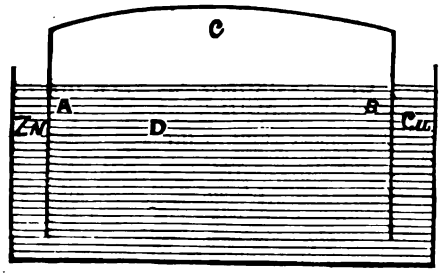


Fig I

By means of the apparatus shown in Fig. I. a weak current can be passed through the soil. The strength of the current will vary with the amount of organic acids in the soil. A series of experiments were conducted with the object of finding out whether these weak currents would in any way affect the growth of seeds and plants. In order that there could be good comparative tests, a number of glass vessels were obtained all of the same size, filled with similar soil, and exposed to the same conditions, such as temperatures and sunlight. In some of these were placed earth plates, as shown in A (Fig. II.), whereas the others only contained the soil. They

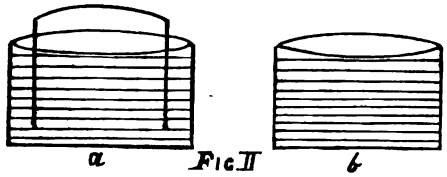


Fig II

were watered each day at the same time and with equal quantities of water. Various seeds were obtained, and the same number of seeds sown in both vessels at the same time and under the same conditions. In all cases the seeds grew very much quicker in the vessels containing the earth plates. In the case of hemp seed it was fully an inch above the surface before there was any sign of it in the ordinary vessels.

Larger plates have been made connected as before and buried in the ground a few feet apart. In these larger experiments the same results were obtained. Seeds were sown in drills as shown in Fig. III. Those in the zones, *a*, *b*, *b'*, were the first to appear. Next came those in the zones *c* and *c'*. Those sown at *d* and *d'* came up nearly a week later than the others.

In order to vary this experiment the earth plates were next buried where *d* was, and fresh seeds sown. The greatest fertility was then noticed to be in the neighbourhood of *d*, that is to say, between the two plates.

With regard to plant life experiments are now being conducted, but so far no distinct difference has been noticed in the case of those under ordinary conditions and those with the earth plates. If the soil is watered with a little very dilute acetic acid the growth of the seeds is much quicker in the case of the earth plates, but no difference is noticed in the ordinary vessels. The latter

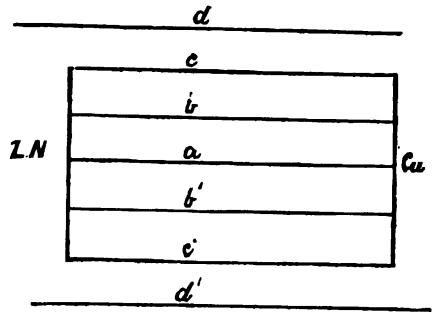


Fig. III

result is probably due to the slight increase in the strength of the current due to the action of the acetic acid.

These earth plates are hardly practicable on a large scale, but might be used in frames or for forcing under glass.

3, Queen's Parade, Brandon Hill, Bristol,
January 16, 1892.

EXAMINATION OF INKS.*

By OSW. SCHLUTTIG and G. S. NEUMANN.

A. *Inks of Class I. Prepared with Iron and Galls.*

Preliminary Test.—The bottle is opened carefully without shaking, 15 to 20 c.c. of ink are drawn out with a pipette, the bottle being immediately closed again with a cork, air-tight, but so that it can be afterwards uncorked again without shaking. The bottle is then left standing quietly for three days at a temperature of 15°.

Meantime a *type* is prepared of the same colour as the ink under examination. A normal ink is first obtained as follows:—23·4 grms. tannin and 7·7 grms. crystalline gallic acid are dissolved in hot water at 50°, and to this solution, diluted as far as convenient, there is added a solution of 10 grms. gum arabic, and further 10 grms. of "officinal" hydrochloric acid (containing 2·5 grms. HCl), a solution of 30 grms. ferrous sulphate, and 1 grm. carbolic acid. The whole is well mixed and diluted to 1 litre; it is then allowed to stand for at least four days at 10—15°, when the clear solution is drawn off from the slight deposit formed. Filtration through paper is to be avoided as much as possible in the examination of inks. If it is unavoidable a fine filter-paper must be used which will absorb merely a trace of tannin. This normal ink is then brought to the exact tone of the ink in question by the addition of suitable colouring matters, using as a standard the 15 c.c. first taken out of the bottle.

The colours used by the authors were:—

Blue—Bayrisch blue D.S.F. of the Berlin Company for Aniline Colours.

Red—Nacarat S from the same works.

Green—Acid green V.B.S.Po. of K. Oehler, of Offenbach.

Brown—Chestnut brown from the same works.

* Treatise by Zahn and Jaensch, *Zeit. fur Analyt. Chemie.*

For instance, we may obtain a type of medium intensity with—

Blue.	Green.	Red.	Black.	
2·2 grm.	1·0	—	2·5	Blue.
—	2·5	—	0·5	Green.
—	—	2·5	—	Red.
—	—	—	3·5	Brown, per litre.

By increasing or diminishing the additions of colouring matters and by combining these various types, all required shades may be obtained.

After three days the bottle is carefully uncorked, and without shaking fully 50 c.c. are taken out of the middle of the liquid with a pipette and filtered through a small folded filter of the finest white filter-paper, taking care that the filtrate does not come in contact with the oxygen of the air more than necessary. Of the filtrate we take exactly 25 c.c. to test its *permanence in glass*. 25 c.c. are let flow into a clean and dry bottle holding 500 c.c. It should be of a cylindrical form, 185 m.m. high and 72 m.m. in diameter, with a flat bottom. The bottle is loosely covered with a cap of filter-paper to exclude dust. The bottle, in which the liquid stands at the depth of about 12 m.m., is allowed to stand for several days at the ordinary temperature of a dwelling-room, is free from ammonia and acid and in diffused light, and is observed. If the bottle is raised up in the hand, shaking must be avoided, as it might cause any film or scum formed on the surface of the liquid to sink to the bottom and be mistaken for a sediment. If at the end of fourteen days any separation takes place, whether on the surface, on the sides of the bottle, or at the bottom, the ink is to be pronounced unsatisfactory from want of permanence.

The type prepared from pure materials remained when submitted to this test three weeks entirely unaltered; there then was formed on the surface of the liquid a film which, even after the lapse of six weeks, was but insignificant. At the beginning of the fourth week a few small points like spots were to be seen at the bottom.

Test for Darkening on Paper.

For this purpose there are used the 15—20 c.c. of unfiltered ink first taken out of the bottle. The test is executed with stripes of ink produced as follows:—A piece of the best white writing paper is stretched tightly and smoothly in a frame placed at an angle of 45°; 0·6 grm. of the ink in question is taken up in a pipette 250 m.m. in inner width and 250 m.m. in length; the mark is at 62 m.m. from the lower end. The pipette is held perpendicularly to the paper, and the ink is allowed to flow out without air-bubbles. There is thus formed a stripe of ink about 6 m.m. wide, and in length, in the author's apparatus, 270 m.m. Such stripes are made side by side with the ink in question and with the type both in their original state, and after each has been diluted with an equal volume of water, in each case three or four times alternately. The frame with the paper is left in its position until the ink has become completely dry upon the paper. The paper is then taken off and left at the common temperature for eight days in air free from dust and acidity and in diffused light. This time is necessary for completing the process of oxidation of the ink. The stripes of undiluted ink are then especially used for judging of the fluidity, the penetration, and the glutinousness, whilst those with the dilute ink serve merely to show the subsequent darkening. If it appears that the dilute ink has not darkened in eight days as much as the dilute type, the ink is pronounced unsatisfactory and no further trial is needed. If the stripes of ink have taken as dark a colour as those of the type, the paper is cut into slips across the direction of the stripes so as to form bands of 3 c.m. in width. One of them is steeped in distilled water, a second in alcohol at 85 per cent, and a third in alcohol at 50 per cent, and allowed to lie for two days. They are then taken out, dried at the common temperature, and the intensities of the residual stripes of the ink in question and of the type are compared. If the ink is satisfactory the stripes on all the three bands must be as dark as the corresponding stripes of the type.

Examination of Fluidity, Penetration, and Adhesiveness.

The fluidity of an ink is best judged by writing with it. It must also be considered that the point of commencement of the stripes obtained as above described has an oval expansion, and the stripe is then nearly equally broad. In inks which flow from the pen too readily the beginning point is very broad and the stripe then narrows downwards.

Whether an ink strikes through the paper is seen by trial-writing.

For testing an ink for its adhesiveness it is necessary to write upon normal paper with the ink in question as well as with the type. The adhesiveness after drying is compared by the application of the hand or of a piece of paper.

(These tests are, of course, not applicable to inks such as vanadium ink, chrome ink, &c.).

I. THE IODATION OF *p*-BROMOBENZOIC ACID. II. SALTS OF *p*-BROMO-*m*-NITROBENZOIC ACID.*

By OLIVER HOUGH.

IT is stated by Weselsky (*Annalen*, clxxiv., 99) that the method of iodation recommended by him is not applicable in the case of bromobenzene or benzoic acid. Believing that possibly a different result might be obtained with bromobenzoic acid, in which two hydrogen atoms are replaced by different substituents, the following experiments were made:—

1. Ten grms. of *p*-bromobenzoic acid, dissolved in alcohol, were heated with the calculated amounts of iodine and mercuric oxide. The product was heated with an aqueous solution of sodium carbonate, and filtered while hot. Hydrochloric acid was added to the cold solution, and the liberated organic acid converted into its barium salt. Analysis showed it to be the barium salt of *p*-bromobenzoic acid. The iodation had not been effected.

2. It was suggested that possibly the iodation had really occurred, but that the sodium carbonate had again removed the iodine. To ascertain whether such was really the case, the acid, after treatment, was digested immediately with barium carbonate. The resulting salt proved to be *p*-bromobenzoate of barium.

3. A third experiment was equally fruitless. Finally, the *p*-bromo-acid, in alcoholic solution, was heated together with iodine and mercuric oxide, in a sealed tube. The temperature of the oven was 150° C. Iodine was not introduced into the acid even in this way.

II. SALTS OF *p*-BROMO-*m*-NITROBENZOIC ACID (M.P. 199° C.)

The known salts of this acid are those of barium, magnesium, and silver. The following are new:—

The *potassium salt* forms yellow coloured prismatic needles, varying in length from one-half to one inch. One hundred parts of water at 26° C. dissolve 33·44 parts of the salt. The salt is anhydrous.

The *sodium salt* crystallises in needles. It contains one molecule of water of crystallisation; 100 parts of water at 26° C. dissolve 16·01 parts of the salt.

The *ammonium salt* separates from aqueous solutions in anhydrous needles; 100 parts of water at 26° dissolve 12·22 parts of the salt.

The *strontium salt* consists of minute white needles. It

* Read at the Chemical Section of the Franklin Institute, October 20, 1891.

contains 3½ molecules of water of crystallisation. Found 14·88 per cent Sr instead of 15·10 per cent; 100 parts of water at 26° dissolve 0·88 part of the salt.

The *calcium salt* consists of white needles. The air-dried salt lost, when carefully heated in an air-bath at 160°, 30·25 per cent of water, corresponding to thirteen molecules. Found 7·45 per cent Ca instead of 7·54 per cent; 100 parts of water at 26° dissolve 1·09 parts of the salt.

The *zinc salt* crystallises in white needles; 100 parts of water at 24° C. dissolve 0·70 part of the salt. The addition of zinc chloride to a solution of potassium nitrobromobenzoate, produced a white precipitate which crystallised from hot water in round yellow coloured masses. Under the microscope these appeared to consist of bundles of little plates. An analysis of the salt showed it to be the basic zinc salt. It contains three molecules of water. Found zinc = 20·24 per cent instead of 19·87 per cent.

The *mercury salt* is anhydrous and white in colour; 100 parts of water at 26° dissolve 0·96 part of the salt. Found Hg = 44·04 per cent instead of 44·90 per cent.

The *nickel salt* crystallises in light green coloured crusts; 100 parts of water at 26° dissolve 1·47 parts of the salt. It contains 2½ molecules of water.

The *cobalt salt* consists of pink needles. It contains three molecules of water; 100 parts of water at 26° C. dissolve 1·05 parts of the salt. Found 11·53 per cent Co instead of 10·74 required.

I carried out the above work in the laboratory of Dr. Edgar F. Smith, University of Pennsylvania.

DISTRIBUTION OF TITANIC OXIDE UPON THE SURFACE OF THE EARTH.*

By F. P. DUNNINGTON,
University of Virginia, Charlottesville, Va.

At the Ann Arbor meeting of the Association for the Advancement of Science in 1885, I read a short paper (*Proceedings A. A. A. S.*, xxxiv., 132), which considered the occurrence of titanic oxide in considerable amount in certain soil of Albemarle Co., Va.; and in an article published (*Amer. Chem. Journ.*, x., 36) in 1888, by Mr. J. F. McCaleb and myself, we presented estimations of this substance in sixteen specimens of soil from scattered points of the United States.

In view of the unfrequent mention of this element as a constituent of rocks and the very rare mention of its occurrence in soils, I have endeavoured to secure samples of soil and some rocks from points scattered over the earth's surface; and, including the before mentioned sixteen, I herewith present the results of examining eighty specimens.

The method employed in the recent determinations is the following:—Weigh into a platinum crucible 1 grm. of the powdered sample, ignite, again weigh, then moisten with water, and add 2 or 3 c.c. of hydrofluoric acid,† gradually heat to dryness, add about 7 grms. of sodium acid sulphate, gradually heat to low redness for one or two hours, cool, digest in 5 per cent diluted sulphuric acid for several hours, filter; to filtrate (method of A. Weller, *Ber. Deutsch. Chem. Gesell.*, xv., 2592), add about 1 c.c. of hydrogen peroxide solution and compare the colour so produced with one similarly obtained from a standard solution of titanic oxide.

To present a more satisfactory comparison with the amount of titanic oxide in the rocks, the percentage on the ignited soil is given together with that on the air-dried soil.

Nos. 1 to 12 are all from Albemarle Co., Va. 1 is dark red clay, from Carter's mountain, farm of Rev. J. T. Randolph being the soil from which was formed a fulgerite (?) which first drew my attention to this occurrence of titanic oxide. 2, deep red clay, one mile south of 1. 3, red clay, one mile north of 1. 4, red clay, one half mile west of 1. 5, light red sand, one mile north-west of 1. 6, red bottom soil, one and one half miles north-west of 1. 7, white micaceous soil, near McCormic Observatory, University Va., and three miles west of 1. 8, near chemical laboratory of University Va. 9, mica schist, one half mile north of 8. 10, deep red clay, ten miles south-west of 1. 11, red clay, ten miles west of 1. 12, Diorite, the rock which is most common in the above locality.

Nos. 13 to 17 are from other points in Virginia. No. 13 is deep red clay from farm of Mr. J. Shelton, Lowesville, Nelson Co. No. 14 a dark grey clay from swamp on Rappahannock River in Stafford Co. No. 15, a grey sandy loam, near Williamsburg, James City Co. No. 16, a yellow clay, per Mr. F. P. Brent, Onancock Creek, Accomac Co. No. 17, white sea-sand, from Virginia Beach, Princess Anne Co. The percentage of titanic oxide found in these respectively is as follows:—

Air-dried.	Air-dried.	Air-dried.	Ignited.
1. 5·42	7. 0·77	13. 1·87	
2. 1·45	8. 2·86	14. 0·88	
3. 2·73	9. 1·14	15. 0·49	0·50
4. 2·73	10. 1·86	16. 0·80	0·84
5. 0·33	11. 1·51	17. 0·07	0·07
6. 1·73	12. 1·15	Average 1·57	

Nos. 18 to 40 are from other portions of the United States. 18, a light brown loam, per Dr. A. C. Hopkins, Charlestown, W. Va. 19, a grey loam, per Mr. J. W. Rinehart, Foote, Mineral Co., W. Va. 20, pale red loam, a "limestone soil," per Mr. C. C. Councilman, Worthington's Valley, Baltimore Co., Md. 21, a grey yellow loam, per Dr. Simon Gage, Cornell University, N.Y. 22, a gritty yellow loam, per Dr. F. P. Venable, Chapel Hill, N.C. 23, a light yellow clay, one foot deep, per Mr. R. M. Cooper, near Black River, Sumter Co., S.C. 24, a grey clay, per Dr. P. S. Baker, over Carboniferous Limestone, Greencastle, Ind. 25, a grey clay, per Dr. W. A. Noyes,* Terra Haute, Ind. 26, a deep orange clay subsoil, per Prof. C. E. Wait, Knoxville, Tenn. 27, a pinkish china clay from a ten foot seam, and 28 a coarse grey clay from an eighteen foot seam, both per Mr. W. R. Searcy, Tuscaloosa, Ala. 29, a heavy grey clay, per Mr. A. P. Wright, river bottom soil, Bolivar Co., Miss. 30, light red surface loam, and 31 a grey sub-soil, both per Mr. Thos. Dunnington, Pine Bluff, Ark. 32, a brown clay, six feet deep, per Prof. W. H. Echols, Rolla, Mo. 33, a pale grey loam, per Dr. F. W. Traphagen, Deer Lodge, Montana. 34, a grey alkaline soil, from Truckee Valley, Nevada. 35, a yellow surface clay, per Dr. Masser, Los Angeles, Cal. 36, a brown clay, three feet deep, per Prof. H. E. Storrs, Los Angeles, Cal. Nos. 37 to 40 were sent by Prof. E. W. Hilgard, Berkeley, Cal. 37, upland red loam Station No. 1226, from Yuba River near Smartsville. 38, yellow grey Mesa soil, Station No. 1281, from Chino Ranch Station, San Bernardino Co. 39, "Red Mountain Land," Station No. 188, from a vineyard in Sonora Co. 40, a red loam, Station No. 1110, Thermolite Colony, Butte Co.

The percentage of titanic oxide found in these, respectively, is as follows (see Table next column).

Nos. 41 to 45 are from Oceanica and Asia. Nos. 41 to 45 were sent by Prof. A. B. Lyons, Oahu College, Hawaii, Sandwich Islands. 41, a dark brown loam. 42 and 43, a yellow brown loam. 44, a brown clay. 45, a grey brown loam. 46, a light grey china clay, and 47 a grey china clay, both per Miss Mildred Page, Tokio, Japan. No. 48, a piece of a grey brick from the Great Wall of China, per Rev. Col-

* From the *American Journal of Science*, vol. xlii., Dec., 1891.

† This acid was used before seeing the article of Dr. Noyes in *Journ. Anal. Chemie*, v., 39

* Dr. Noyes writes that he has recently found from 0·5 to 4 per cent of titanic oxide in a number of minerals from Arkansas.

	Air-dried.	Ignited.		Air-dried.	Ignited.
18.	0·83	0·88	30.	0·52	0·62
19.	0·88	0·98	31.	0·60	0·62
20.	1·17	1·26	32.	0·57	0·65
21.	0·55	0·58	33.	0·44	0·50
22.	0·49	0·55	34.	0·57	—
23.	0·57	0·61	35.	0·72	0·82
24.	0·71	0·76	36.	0·49	0·53
25.	0·58	0·62	37.	0·77	0·85
26.	0·46	0·50	38.	0·72	0·75
27.	1·01	1·12	39.	4·93	6·05
28.	0·67	0·76	40.	0·90	0·97
29.	0·46	0·61	Average	0·85	0·98

lins Denny. 49, a pink clay, and 50 a yellow loam subsoil from the bank of the Yellow River, and 51 a fine yellow silt from the old bank of the Yellow River. The three last specimens were sent by Dr. Edgar Woods, Tsing-Kiang-Pu, China. 52, light red pottery, from Kurrachee, Sind, India. 53, dark brown crucible clay, and 54 red furnace clay, both from Tumkur, India. The three last specimens were sent by H. B. M.'s Secretary for India. 55, grey loam from the shore of the Sea of Galilee, Palestine, per Rev. Collins Denny, of Vanderbilt University.

The percentage of titanic oxide found in these respectively is given below, and in making an average the specimens 41 to 45 are counted as one.

	Air-dried.	Ignited.		Air-dried.	Ignited.
41.	4·43	5·25	49.	0·58	0·68
42.	2·40	3·37	50.	0·60	0·65
43.	2·25	3·11	51.	0·54	0·56
44.	4·00	4·64	52.	0·69	—
45.	2·78	3·37	53.	0·62	0·73
46.	0·70	0·80	54.	0·28	0·30
47.	0·40	0·50	55.	1·80 (?)	1·90
48.	0·55	0·55	Average	0·90	1·18

Nos. 56 to 72 are soils from Europe. Nos. 56 to 62 are from Russia, and were sent by Prof. Nich. Menschutkin, Kaiser University, St. Petersburg. 56 is a yellow sandy loam, "Souglinok," from Borovitsky, Novgorod. 57, dark grey loam, Prof. Docoutschaeff's type, "Solonetz" (barren black earth), Prilouky, Poltava. 58, brown grey loam, forest soil, Zenkovsky, Poltava. 59, dark grey loam, "Tschernosem" (black earth), Prilouky, Poltava. 60, sandy black earth, "Tschernosem," Zenkovetsky, Polkava. 61, black earth, "Tschernosem," Balashoff, Saratoff. 62, black earth, "Tschernosem," Zoubrilovka, Saratov. 63, white porcelain clay from Halle, Prussia. 64, white porcelain clay from St. Yrieux, near Limoges, France. 65, yellow grey loam from Florence, Italy, per Dr. C. L. Minor, of New York. Nos. 66 to 72 are from Great Britain, and were collected for me by Prof. W. G. Brown, of Lexington, Va. 66, black garden soil, Kensington, London. 67, dark grey loam from coast near Brighton. 68, grey loam, Liverpool. 69, grey sandy loam, Donnington, Lincolnshire. 70, grey sandy loam, Cambridge. 71, brown yellow clay, Inversnaid, Loch Lomond, Scotland. 72, brown clay under Forth Bridge, N. Queensferry.

The percentage of titanic oxide found in these, respectively, is as follows:—

	Air-dried.	Ignited.		Air-dried.	Ignited.
56.	0·54	0·57	65.	0·53	0·62
57.	0·40	0·43	66.	0·21	0·27
58.	0·60	0·70	67.	0·46	0·52
59.	0·32	0·34	68.	0·41	0·46
60.	0·58	0·66	69.	0·45	0·49
61.	0·63	0·79	70.	0·50	0·53
62.	0·56	0·73	71.	0·85	0·89
63.	0·03	0·03	72.	2·36	2·52
64.	0·015	0·017	Average	0·54	0·62

This wide distribution of titanic oxide naturally suggests the examination of the rocks themselves. I have so far been able to examine only the following typical rocks, the localities of which have furnished also the samples for analyses already published: 73, Trachyte, Kühlsbrunnen; 74, Trachyte; 75, Trachyte, Drachenfels; 76, Hornblende andesite, Wolkenburg. These four were from the Siebengebirge. 77, Gabbro, Radauthal, Harzburg;* 78, Melaphyr, Ilmenau, Schneidemuller-berg; 79, Melaphyr, Plauenschen Grunde, near Dresden; 80, Nosean phonolite, Castle Olbrück, Laacher See. These afford the following:—

	TiO_2 mentioned in published analysis.		TiO_2 found.
73.	None	Zirkel, II., p. 181	0·22
74.	,,	,, p. 182	0·86
75.	0·38	,, p. 181	0·64
76.	None	,, p. 212	1·14
77.	,,	,, p. 116	0·10
78.	0·89	,, p. 55	1·01
79.	Trace	Zirkel I., p. 584	0·36
80.	None	,,	0·18
		Average ..	0·56

While the frequent association of titanium with iron (as indicated by the colour after ignition) in these soils points to menaccanite as a source of the titanic oxide, yet the considerable amount of this substance in some of the clays and rocks containing little iron suggests that it may also result from titanite, which has been observed (Dana's "System of Mineralogy," p. 389) to be widely distributed in igneous rocks.

In conclusion, I desire to thank those who have assisted me in this work by supplying the desired specimens.

THE OXIDATION OF METALLIC ARSENIDES BY THE ELECTRIC CURRENT.†

By LEE K. FRANKEL.

(Concluded from p. 57).

Orpiment (As_2S_3). — The preliminary investigations made with this mineral showed that it came under the same category as the metallic arsenic. When the finely powdered mineral was introduced into the molten caustic potash, a volatilisation of the arsenic, recognisable by its odour, occurred. The precautions given under metallic arsenic regarding the cooling of the caustic potash and the regulation of the current were then introduced with successful results. Some difficulty may at first be experienced in obtaining correct control of the operation, but a few oxidations will give the operator sufficient experience to bring the decomposition to a successful completion. The conditions best adapted for the work are a current of 1 ampère, 25—30 grms. of caustic potash, the current being allowed to run for thirty minutes. Using these conditions, no arsenic was found in the slight residues which remained after decomposing the fusion, nor was any odour of arsenic perceptible during the entire course of the operation.

0·1443 grm. of orpiment decomposed according to the directions gave 0·1761 grm. of magnesium pyroarseniate = 59·08 per cent arsenic.

0·1044 grm. of orpiment yielded 0·12805 grm. magnesium pyroarseniate = 59·38 per cent arsenic.

0·2233 grm. of the same ore dissolved in nitric acid and weighed as magnesium pyroarseniate in a platinum crucible yielded 0·2755 grm. of magnesium pyroarseniate = 59·72 per cent arsenic.

Proustite (Ag_3AsS_3).—But a very small quantity of the mineral was available for analysis, and even that was intimately mixed with argentite. No attempt was there-

* I find in Bischoff, iii., p. 467, Gabbro from Rodanthal bei Steinbruch, contains TiO_2—1·75 per cent.

† Read at a meeting of the Chemical Section of the Franklin Institute, November 17, 1891.

fore made to extract the former mineral by hand-picking, but the entire mixture was placed in an agate mortar and ground, the grindings then being passed through a sieve. This removed all the proustite with some of the argentite, the greater portion of the latter remaining behind as flattened plates. Sufficient argentite, however, remained with the proustite to reduce in a considerable measure the percentage of the arsenic, and the deviation of the results from the theoretical percentage is attributable to this cause. Sufficient material was not at hand to make a check analysis by dissolving the mineral in nitric acid and determining in the usual way, but as the residues were most carefully examined for arsenic, and as none was found to be present, the natural conclusion arrived at was that the decomposition was complete. No loss of arsenic was noticeable during the entire operation, and the closeness of the results indicates that the decomposition of this mineral by the electric current can be accomplished as successfully as any one of those previously described. The conditions for oxidation were as follows :—A current of 1 ampère running for thirty minutes, the current being reversed during the last five minutes. The amount of caustic potash used was 25—30 grms. Below will be found the results obtained :—

1·1589 grm. of proustite weighed as magnesium pyroarseniate in a porcelain Gooch crucible gave 0·0147 grm. of magnesium pyroarseniate = 4·48 per cent arsenic.

0·2255 grm. of proustite yielded 0·0249 grm. of magnesium pyroarseniate = 5·34 per cent arsenic.

Besides these minerals already recorded several others were subjected to oxidation by the current, but owing to lack of material for the continuance of the work, satisfactory conclusions were not reached. The results are, however, of interest, and are, therefore, here appended.

Domeykite in Niccolite, $n(Ni.As)+m(Cu_3As.)$. — The mineral used for oxidation came from Michipicoten Island, and was a small section of a specimen in the mineral collection of the University of Pennsylvania, labelled whitneyite. Two oxidations of the mineral, in which the residues still showed arsenic, gave, to the surprise of the author, 35·3 per cent and 40·04 per cent of arsenic respectively, showing that the mineral could not be whitneyite, since this should contain theoretically 11·64 per cent of arsenic. A later oxidation gave, using 0·2207 grm. of the mineral, 0·2016 grm. of magnesium pyroarseniate = 44·22 per cent arsenic. 25—30 grms. of caustic potash were employed, with a current of 1 to 1½ ampères, for thirty minutes, reversing the current at the end for five minutes. In this oxidation no trace of arsenic was found in the residue. On reporting the results obtained to Dr. Koenig, he made an analysis of another sample by dissolving the mineral in nitric acid, and found it to contain 47 per cent of arsenic. This result is, however, not inharmonious with the last one obtained by the current, since, in a fresh fracture of the mineral, the niccolite and domeykite can be seen lying alongside of each other. Owing to this non-homogeneity, the sample analysed by Dr. Koenig may have contained more niccolite than the one used for oxidation by the current, and gave proportionately a higher percentage of arsenic. Unfortunately, the scarcity of the mineral necessitated the discontinuance of the work, and the question of complete oxidation is still in doubt. The few per cent difference in the results obtained by the two methods, however, indicates that the decomposition can be successfully accomplished under the conditions mentioned above.

Enargite ($3Cu_2S.As_2S_5$).—The material used for decomposition contained an admixture of gangue, and as with the domeykite, not sufficient of the substance was obtainable to settle thoroughly the question of oxidation. As the percentage of arsenic found, however, is within the neighbourhood of what the mineral ought to contain, and as no arsenic was detectable in the residue from the fusion, the result obtained is here appended without any definite statement regarding the thoroughness of the method. The amount of caustic potash used in the oxidation was 25—30 grms., the current strength 1 ampère, with a reversal of the current at the end of the operation for five minutes. The arsenic was determined by weighing as magnesium pyroarseniate on a porcelain Gooch crucible.

0·2840 grm. of enargite gave 0·0770 grm. of magnesium pyroarseniate = 13·12 per cent arsenic.

The theoretical percentage of arsenic in the mineral is 19·1 per cent. If we remember, however, that the sample used contained gangue material, and that no arsenic was found in the residue, it is but fair to assume that the result lies within the limits of error, and that the oxidation is complete. No positive statement, however, can be made.

A study of the methods used for the determination of the arsenic in the various oxidations will be of interest. As has already been stated, the determination of the arsenic as arsenious sulphide by weighing on a porcelain Gooch crucible cannot be recommended owing to the great difficulty experienced in removing the sulphur with which the precipitate of arsenious sulphide is contaminated. The more common method of weighing the arsenic as magnesium pyroarseniate was found to be accurate if the conditions laid down for this determination are complied with, the method requiring at the same time great care. In the incineration of the filter from the magnesium ammonium arseniate constant vigilance was required to prevent a volatilisation of a portion of the arsenic, even though the filter had been previously saturated with a concentrated ammonium nitrate solution. And in many cases it was necessary to moisten the burnt filter several times with the solution before it could be completely reduced to ash. Weighing the precipitate on either a platinum or porcelain Gooch crucible removes these sources of error, and is, of all the methods so far mentioned, the most to be recommended. In the precipitations with magnesia solutions, it was noticed that the presence of large quantities of alkaline salts have a tendency to materially retard the precipitation of the magnesium ammonium arseniate, and it became necessary to allow the solution to stand at least forty-eight hours before the precipitation was complete. For this reason, where large quantities of alkaline salts are known to be present,—for example, the caustic potash used in the fusion,—it may be more advisable to reduce the arsenic with sulphurous acid, precipitate it as arsenious sulphide, filter and wash, and then re-convert it into arsenic acid and determine as magnesium pyroarseniate.

Owing to the time and care required in the above determinations, the method described in "Sutton's Volumetric Analysis," Sixth Edition, as recommended by Pearce, of the Colorado Smelting Company, was tried. The substance of the method is as follows :—"The arsenic brought into the form of alkaline arseniate is acidified with nitric acid, and boiled to remove carbon dioxide and nitrous fumes. It is then cooled to the ordinary temperature, and almost exactly neutralised as follows :—"Place a small piece of litmus paper in the liquid; it should show an acid reaction; now gradually add strong ammonia until the litmus turns blue, avoiding a great excess. Again make slightly acid with a drop or two of strong nitric acid, and by means of very dilute ammonia and nitric acid, added drop by drop, bring the solution to such a condition that the litmus paper, after having previously been reddened, will, in the course of half a minute, begin to show signs of alkalinity. The litmus paper may now be removed and washed, and the solution, if tolerably clear, is ready for the addition of silver nitrate. If the neutralisation has caused much of a precipitate (alumina, &c.), it is best to filter it off at once to render the subsequent filtration and washing of the arseniate of silver easier, "——." The latter portion of the process consists in determining the silver in the silver arseniate and calculating the percentage of arsenic from the amount of silver found.

A number of determinations were made by the author to ascertain the value of the method, but all of the attempts made resulted in failure. It was found well nigh impossible to tell by the colour of the litmus paper whether the solution was acid or alkaline. In several cases methyl orange was used as an indicator, and while the solution was made slightly alkaline, as recommended by Pearce, the addition of ammonia to the filtrates invariably brought down considerable quantities of silver arseniate, and the results obtained were proverbially low. The silver was not determined by titration, as recommended by Pearce, but by electrolysis. The best result obtained by this method, with the details of the operation, are given below.

A sample of rammelsbergite was decomposed under the conditions mentioned for that mineral. The fusion was decomposed with hot water, the insoluble material filtered off, and the clear filtrate acidified with nitric acid and boiled to remove the carbon dioxide. On cooling, ammonium hydroxide was added, the precipitated alumina, &c., filtered off, and the additions of dilute nitric acid and dilute ammonia made according to Pearce's direction, until the solution became faintly yellow, methyl orange having been used as an indicator. Silver nitrate was now added, the solution stirred, and the precipitate of silver arseniate filtered off. The addition of a drop of ammonium hydrate to the clear filtrate gave a further precipitation, and ammonia was therefore added until the precipitation was supposed to be complete. The two precipitates were then united, washed with cold water, dissolved in nitric acid, and the excess of acid evaporated. To the solution ammonium hydrate was added until the solution became alkaline, and then an excess of potassium cyanide, the solution electrolysed, and the resultant silver weighed. 64·21 per cent of arsenic was found, the same sample giving, by the pyroarseniate method, 70·34 per cent arsenic.

The author believes that with continued practice, sufficient dexterity might be obtained with the method to obtain accurate results, but it is hardly one that could be recommended for work outside of a technical laboratory, where absolute accuracy is not so essential a feature as that the results should be correct, relatively, to each other.

A comparison of the oxidation of the metallic sulphides with that of the metallic arsenides shows several points of difference. In the oxidation of the sulphides, it was observed by Dr. Smith that the process took place in three stages, the sulphur being first oxidised to hydrogen sulphide, then to sulphurous acid, and eventually to sulphuric acid. A similar state of affairs was not observed with the arsenides, and the oxidation evidently proceeds directly from metallic arsenide to arsenic acid. Even in samples where the oxidation had not been complete, and where the residues still showed undecomposed material, the filtrates from the fusion showed no trace of arsenious acid after the alkaline arseniate had been removed by precipitation with magnesia solution.

In conclusion, the author would here express his sense of deep obligation to Dr. Edgar F. Smith for his unremitting kindness during the progress of the above work, and for his constant help in assisting its completion.

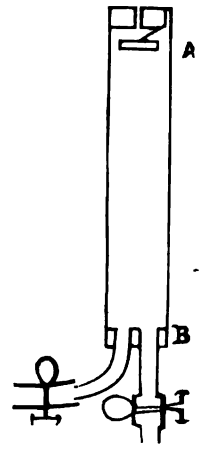
Thanks are also due to Dr. George A. Koenig for samples of minerals, and to Mr. D. L. Wallace, of this laboratory, for assistance rendered in the oxidations.

APPARATUS FOR MEASURING LIQUIDS QUICKLY.

By ALEX. F. REID, of Bonshaw, Stewarton, N.B.

Some years ago I wrote an article (Chem. News, vol lvii., p. 39) on measuring liquids by drops. This was a somewhat slow method of measuring out liquids, except when small quantities were taken. It is made use of very effectively by Dr. Bond, of Gloucester, in his acidometer for determining the acidity of milk, whey, &c. He uses a standard solution of caustic potash, with phenolphthalein as indicator. The milk or liquid to be tested is measured out in a piece of glass tubing up to a certain mark, and delivered into a small vessel. The caustic potash solution is dropped from a small dropping tube till the desired pink tint is produced, the number of drops corresponding to the degree of acidity.

The apparatus I am about to describe is on a larger scale. In some laboratories many solutions have to be measured out, and to do this quickly is much to be desired. The following apparatus, which can easily be made, I find very serviceable in rapidly measuring out definite quantities of liquid :—



A piece of glass tube, A, B, is taken, and a cork is inserted in each end. Through the top cork a small hole is bored ; this is closed on the under side by a valve of indiarubber cloth with a piece of cork attached to it. Through the bottom cork are bored two holes of about equal size, through which are passed two glass tubes. Two clips are attached to two pieces of indiarubber tube at the end of each of these glass tubes, as shown in the figure. The liquid is run into the apparatus through one of these tubes from a reservoir by opening the clip. The liquid rises up and lifts the piece of cork, thereby closing the valve. There is now the desired quantity of liquid in the apparatus, which can be run out by opening the other clip, the valve meanwhile falling down, as shown in the figure, ready to let the air escape in filling again.

The same apparatus makes a good burette if the tube A B is graduated and a little longer, as no time is lost in filling it to zero. It can thus be worked very quickly.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

Up to within the last year, the estimation of iron and aluminum in the presence of large quantities of phosphoric acid has always been attended with great difficulties, it being impossible to obtain results which approximated to the actual amounts of these bases present, or even agreed among themselves.

It was in connection with some analyses of phosphatic rocks in the work of the Chemical Division of the Department of Agriculture that my attention was first drawn to

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 12.

this subject last spring, and I was directed by the chemist to make a thorough study of all the methods proposed for this work. In the following paper is found a *resumé* of the work I have done in this line. I will first give an abstract of the various methods which have been proposed.

The one which has been most generally used, and which is at the same time the most inaccurate, is conducted as follows:—

200 c.c. of a hydrochloric acid solution (=4 grms. material) are taken, and ammonia added to alkaline reaction. Care must be exercised not to add too great an excess, or time will be wasted in boiling it out. The ammonia precipitates the iron and aluminum together with the phosphoric acid. Boil the solution until the vapours are no longer ammoniacal. Allow the precipitate to settle, and decant the clear fluid on a filter. Wash with 50 c.c. of boiling water, stir, allow to settle, and decant as before. As some lime and magnesia may be carried down, dissolve in the beaker with as little hydrochloric acid as possible and re-precipitate with ammonia, boiling as before. Wash by decantation three or four times, using 50 c.c. of boiling water each time. Finally transfer to the filter with boiling water, wash free from chlorides, dry in air-bath at 110° C., ignite gently until the paper is burnt, then heat intensely, cool, and weigh.

The weight of phosphoric acid in this precipitate is found by any of the usual methods, preferably the molybdate method, and is deducted from the total weight, the oxides of iron and aluminum being thus found by difference.

Several methods have been elaborated which are based on the previous separation of the phosphoric acid. One of the first of these is that of Sonnenschein.

This method is applicable to all cases in which the phosphoric acid is present as orthophosphoric. The material is dissolved in dilute nitric acid and sufficient molybdenum solution added to precipitate all of the phosphoric acid. The precipitate of ammonium phosphomolybdate is filtered off and washed with a dilute solution of ammonium nitrate. A sufficient excess of ammonium sulphide is added to the filtrate, the molybdenum sulphide is removed by filtration, and the bases separated in the filtrate by means of ammonium hydrate.

This method should theoretically give correct and accurate results, but up to this time it has never been generally used, various analysts reporting their inability to obtain good results. The causes of the failure have never been satisfactorily explained.

Stutzer proposed the following method:—

Precipitate the iron and aluminum as phosphates by means of ammonia, collect on a filter, and wash once with water, then transfer filter and precipitate to a beaker and add 150 c.c. of molybdate solution to cause the separation of the phosphoric acid. Filter, and precipitate the bases in the filtrate by means of ammonium hydrate.

This method should also give good results, but it has been discarded, as in some inexplicable manner it would at times suddenly fail.

Dr. J. H. Vogel has investigated Stutzer's method very thoroughly, and takes the following exceptions to it:—That the addition of such a large amount of molybdate solution is not at all justified, and renders subsequent operations difficult, there being present 75 c.c. of concentrated nitric acid, which must be neutralised before the hydrates can be precipitated with ammonia. The presence of the filter also renders the washing of the precipitate difficult and necessitates a large amount of wash water. He has, therefore, modified the method as follows:—The precipitate of iron and aluminum phosphates is collected on a small filter. It is not washed, and in case the last drops of filtrate do not come through rapidly it is not necessary to wait, but the precipitate may be immediately dissolved, as small quantities of the filtrate do not change the results. The first precipitation of the phosphates by ammonia, according to Glaser (see description of this method), only serve the purpose of removing the bulk of the phosphoric acid, as its presence would necessitate the use of very large quantities of the molybdate solution, and it is, on the other hand, necessary to work with small and concentrated amounts of the liquid. In all his experiments Dr. Vogel found that 50 c.c. of molybdate solution were sufficient. This amount, however, is regulated by the quantity of the precipitate which we have, and must be left to the judgment of the analyst. The 50 c.c. of the molybdate solution are put into a 100 c.c. graduated flask, and about 30 c.c. poured on the precipitate. The strong nitric acid present immediately dissolves the latter. The filter is then washed with the other 20 c.c., which have previously been diluted to 100 c.c. 100 c.c. are always sufficient for washing, and we need not consider any yellow colour present on the filter, as the acid wash water will rapidly remove all the bases. The filtrate and washings are allowed to stand until the phosphoric acid is completely precipitated. The whole liquid is then transferred to a filter and the beaker washed three or four times with a solution of ammonium nitrate, the filter being washed an equal number of times. The filtrate containing the bases is then rendered strongly alkaline with ammonia, and the liquid brought to the boiling-point. It is not necessary to expel the excess of ammonia, as the large amount of ammonia salts present prevents any solution of alumina or precipitation of magnesia. By proceeding in this manner we get a precipitate free from molybdic acid, unless we are working with very large amounts of iron and alumina, in which case the hydrates must be dissolved in dilute hydrochloric acid and reprecipitated with ammonia.

I now come to another modification of the molybdate method which I have used with perfect success, and which has invariably given accurate results both to me and to several other assistants in our laboratory. This modification was first used in this laboratory by Mr. K. P. McElroy, for the estimation of alumina in phosphatic baking powders.

100 c.c. (= 1 grm. substance) of a nitric acid solution of the substance are placed in a 500 c.c. flask, and a solution of ammonium molybdate added until all of the phosphoric acid has been precipitated. The addition of ammonium nitrate will hasten the separation of the ammonium phosphomolybdate. It is best to let the liquid stand over night. It is then made up to the mark, filtered through a dry filter, and duplicate samples of 200 c.c. each of the filtrate taken for analysis. A small quantity of ammonium nitrate is dissolved in the liquid and ammonia cautiously added, keeping the solution as cool as possible. The iron and aluminum will come down as hydrates. They are collected on a filter and washed with water, the filtrate and washings being collected in a beaker. It is usually best to re-dissolve the precipitate with a few c.c. of a solution of ammonium nitrate in dilute nitric acid, re-precipitate with ammonia, filter, wash, ignite, and weigh. This excludes all possibility of error by the presence of molybdic anhydride. After weighing, the oxides may be fused with sodium bisulphate, dissolved in water, and the iron determined volumetrically in the usual manner. My results on as small quantities of material as 0·200 grm. have always been closely concordant. I usually take four portions of 100 c.c. each (= 0·200 grm.); in two of these I determine both oxides gravimetrically, and in the other two I re-dissolve the freshly re-precipitated hydrates in dilute sulphuric acid and determine the iron volumetrically.

(To be continued.)

New Process for the Formation of Amidoalizarin.—Charles Lauth.—The preparation of amidoalizarin β is generally effected by the reduction of nitroalizarin either by means of hydrogen sulphide and ammonia or by means of glucose in presence of sulphuric acid or by means of zinc and potassa. The reduction can be effected as well and very easily by the action of dimethylaniline.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 22nd, 1892.

Prof. O. J. Lodge, F.R.S., Vice-President, in the Chair.

Messrs. J. B. Peace and E. G. Highfield were elected members of the Society.

Prof. G. F. Fitzgerald, F.R.S., read a paper "*On the Driving of Electromagnetic Vibrations by Electromagnetic and Electrostatic Engines.*"

The author pointed out that as the electromagnetic vibrations set up by Leyden jar or condenser discharges die out very rapidly, it was very desirable to obtain some means whereby the vibrations could be maintained continuously. Comparing such vibrations with those of sound he said the jar discharges were analogous to the transient sound produced by suddenly taking a cork out of a bottle; what was now required was to obtain a continuous electromagnetic vibration analogous to the sound produced by blowing across the top of a bottle neck. In other words some form of electric whistle or organ-pipe was required.

These considerations led him to try whether electromagnetic vibrations could be maintained by using a discharging circuit, part of which was divided into two branches, and placing between these branches a secondary circuit tuned to respond to the primary discharge. This did not prove successful on account of there being nothing analogous to the eddies produced near an organ pipe slit. The analogy could, he thought, be made more complete by utilising the magnetic force of the secondary to divert the primary current, first into one of the two branches and then into the other.

If spark gaps be put between two adjacent ends of the branches and the main wire, then the magnetic effect of the secondary current should cause the spark to take the two possible paths alternately. Electrically driven tuning forks and vibrating spirals were cases in which magnetic forces set up vibrations, but here the frequency depended on the properties of matter and not on electrical resonance. The frequency of delicate reeds could, however, be controlled by resonance cavities with which they were connected, and he saw no reason why the same action could not be imitated electromagnetically, using an electric spark as the reed.

Referring to the properties of iron in connection with electromagnetic vibrations, he pointed out that a prism of steel 1 m.m. long had a period of longitudinal vibration of about one-millionth of a second, and as this was comparable with the rates of electromagnetic vibrations, the immense damping effect which iron had on such vibrations might be due to the setting up of sound vibrations in the material.

Other methods of driving electromagnetic vibrations had suggested themselves in the shape of series dynamos or alternators. The polarity of a series dynamo driving a magneto motor would, under certain circumstances, reverse periodically, and thus set up an oscillatory current in the circuit. Similar effects can be got from series dynamos charging cells or condensers. In an experiment made two weeks before with Planté cells and a gramme dynamo, reversals occurred every fifteen seconds.

Greater frequencies might be expected with condensers. The latter case he had worked out theoretically. He had also tried experiments with Leyden jars and a dynamo, but got no result. This might have been expected, for the calculated frequency was such as would prevent the currents and the magnetism penetrating more than skin deep.

Calling the quantity of electricity on the condenser Q, the differential equation for a dynamo of inductance L, and resistance r, and a condenser of capacity X is—

$$L\ddot{Q} + r\dot{Q} + \frac{Q}{X} = \dot{L}\dot{Q}$$

or—

$$L\ddot{Q} + (r - \dot{L})\dot{Q} + \frac{R}{X} = 0.$$

If L be = O the solution of the equation is—

$$Q = Q_0 \varepsilon^{-\frac{r}{L}t} \cos. 2\pi \frac{t}{T},$$

and the rate of degradation of amplitude depends on the factor—

$$\varepsilon^{-\frac{r}{L}t}.$$

If, however, L be greater than r, the exponent of ε becomes +, and hence Q would go on increasing until limited by the saturation of the iron or the increased resistance of the conductors due to heating.

A dynamo without iron, provided one could be made to run fast enough to send a current through itself, would be likely to give the desired effect. The author thought that by making such a dynamo large enough, and its armature very long, it would be possible to get a frequency of about one million.

Electrostatic machines seem, however, to be more promising driving agents. Like series dynamos their polarity depends on the initial charge, and can be easily reversed. Hitherto such machines have been inefficient, mainly on account of the sparking in them, but Maxwell had shown how this could be obviated. There was the same kind of difference between electromagnetic and electrostatic machines as between Hero's engine and the modern pressure engine. Like modern engines, electrostatic machines worked by varying capacity, but the effect of this variation in electrostatic machines was only to vary the frequency and not the rate of degradation.

From the fact that electrostatic multipliers could be driven by alternating currents, he thought they might be made to drive alternating currents. If magnetic currents could be obtained then electrostatic engines would easily be produced.

In conclusion, the author described a modified electrostatic multiplier which he believed offered a feasible solution of the problem. In this machine the collectors were supposed joined to the ends of the vibrating circuit and would, therefore, become + and − alternately. Inductors and brushes were to be so arranged that an insulating cylinder turning between them should have many + and − charges distributed alternately round its periphery. By suitable adjustment these charges could be collected at the proper instants so as to keep up the vibration.

The Chairman, Prof. Lodge, said the paper was very suggestive and full of interesting points.

The subject of electromagnetic vibrations was attracting great attention in America in connection with the Manufacture of Light. Hertz oscillations die out too soon to be satisfactory, for their duration rarely exceeds a thousandth part of the interval between consecutive discharges.

The theory of dynamos charging condensers he considered extremely interesting, and thought the fact that the damping factor could be changed in sign must have tremendous consequences.

Dr. W. E. Sumpner asked a question about a method of doubling frequency of alternation recently described by Mr. Trouton, in which the armature of one alternator excites the fields of a similar machine. Mr. Trouton had said that after once doubling the frequency it was not possible to go on doing so. He (Dr. Sumpner) thought that by adding other machines the frequency could be still further increased, and gave a proof of the fact.

In reply, Prof. Fitzgerald said that adding another machine increased the frequency by a given amount, and

did not double the preceding one. Hence, to increase the frequency a thousandfold a thousand machines would be required, and on this account Mr. Trouton considered it impracticable.

Prof. S. P. Thompson thought the paper very suggestive, and the acoustic analogies very interesting. Melde's apparatus was an instance of doubling or halving a frequency. On reading the title of the paper he had expected hearing of a method of maintaining electromagnetic vibrations by giving occasional impulses in some such may as that in which a tuning fork could be kept vibrating by allowing the hammer of a trembling bell to knock against. There was another method of intensifying electric oscillations which he had seen mentioned in a Patent Specification by Sir W. Siemens, who suggested using a series dynamo with a telegraph cable to augment the signalling currents.

On the subject of ironless dynamos he (Prof. Thompson) desired further information. Some years ago he had made calculations and found the speed at which they would require to run was so enormous as to be beyond the range of engineering possibility.

Mr. C. V. Boys, referring to the author's suggestion of using an electric spark with alternate paths to maintain vibration, said that he had tried whether an oscillatory spark was displaced by a magnetic field, but the displacement even when photographed by a revolving mirror was barely appreciable.

Prof. Perry asked for an explanation of the term "skin deep magnetism." He was not previously aware that Sir W. Siemens had described a method of improving cable signalling by using a series dynamo. He himself had patented a somewhat similar arrangement. He had also made a dynamo without iron, but had not got it to work.

In reply to Prof. Perry the author of the paper said that in electromagnetic vibrations the magnetic force alternates so rapidly that it could not penetrate far into the field magnet of a dynamo before it is reversed; hence the magnetism would only be skin deep.

Dr. Burton suggested that a commutator with many segments, something like that used by Mr. Gordon in his "Researches on Specific Inductive Capacity," might possibly be employed for producing high frequencies."

A communication on "*Supplementary Colours*," by Prof. S. P. Thompson, F.R.S., was postponed.

ROYAL INSTITUTION OF GREAT BRITAIN.

Special General Meeting, Monday, February 1, 1892.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following Address to Her Majesty the Queen, Patron, and His Royal Highness the Prince of Wales, Vice-Patron of the Royal Institution, in reference to the decease of His Royal Highness the Duke of Clarence and Avondale, Honorary Member of the Institution, was read and unanimously adopted:—

"The Members of the Royal Institution of Great Britain, in Special General Meeting here assembled, desire most respectfully to offer to Her Majesty the Queen (Patron of the Royal Institution) and the Prince of Wales (Vice-Patron of the Institution) the expression of their unfeigned sorrow at the loss which Her Majesty, His Royal Highness, and the Nation have sustained by the death of his Royal Highness the Duke of Clarence and Avondale (Honorary Member of the Institution), and they ask to be allowed to tender their heartfelt sympathy and condolence with Her Majesty and His Royal Highness the Prince of Wales in their bereavement."

Letters of regret for non-attendance were read from His Grace the President, the Earls of Derby and Ducie, Sir John Fowler, and many others.

NOTICES OF BOOKS.

Manual of Chemical Technology. By Rudolf von Wagner. Translated and Edited by William Crookes, F.R.S., Past Pres. C.S., and Pres. Institute Electrical Engineers. From the Thirteenth enlarged German Edition, as Remodelled by Dr. Ferdinand Fischer. With 596 Illustrations. London: J. and A. Churchill, 1892. Large 8vo., pp. 968.

The value of this capital work has been most fully recognised, since its thirteenth German edition has already appeared. In accordance with the rapid advance and improvement in the chemical arts, alterations, omissions, and additions have been largely necessitated; a task which has been most ably performed by Dr. F. Fischer. In consequence, the English version of 1872 has to a great extent been superseded, and possesses mainly a historical value. During the last twenty years, new materials have been introduced into commerce, new processes devised, and former materials discarded, as most strikingly exemplified in the tinctorial trades and in the manufacture of colours. One of the chief improvements in the latest German edition, and, of course, in the English version now before us, is a re-arrangement of the subject. Dr. Fischer, in the spirit of the old name given to chemists, "philosophers by fire," gives the first place to fuel, and argues that more intelligent care shall be turned to its utilisation. The interests of the world demand that every pound of coal should be made to yield its utmost share of duty. Hence, we cannot help confessing that England has been, and still is, the foremost transgressor; because we have used it recklessly, wasting in our domestic fires certainly not less than 90 per cent of the heat producible, and generating smoke to a fearful extent. Our readers will remember the solemn execration pronounced upon us by Liebig for the waste of our sewage matter—a crime still committed by all those who either run the sewage direct into the sea, or who precipitate it and then carry it out to sea in barges. But it appears to us that we have equally deserved a similar anathema for our treatment of coal. Dr. Fischer contends in the work before us that "hundreds of thousands of stoves in Germany which have imperfect doors or none at all, allow from 50 to 80 per cent of the entire combustion value of the fuel to pass up the chimney." He is of opinion that no substitute for coal can be thought of.

A peculiarity of this edition are the illustrations, which are excellent, and the lettering for reference is perfectly clear.

A verbatim translation of the original has been in many parts impossible. Passages which refer to conditions existing only in Germany have been, of course, omitted.

The work before us is remarkably comprehensive. It gives an able, accurate, and intelligent survey of the entire extent of chemical industry, with the singular exception of quinine, morphine, and the other medical alkaloids.

As an instance of the different manners in which the laws of Germany and of England respectively interfere with chemical manufactures, we may refer to alcohol. In Germany, spirits for technical (or scientific) purposes are exempt from taxation if they are "denaturised by any one of a variety of methods which the manufacturer may select." The most suitable of all these agents is Dipple's animal oil. In Germany, we see that the Revenue Authorities are not allowed to ride rough shod over the interests of science and manufactures in the manner which is tolerated in "free" England.

The reader may at first sight feel surprised at finding milk, meat, &c., discussed in a work like the present; but, though these substances are certainly natural products, yet their preservation depends on chemical principles. Prof. Neubauer's protest against artificial wine as here quoted from his celebrated "Chemie des Weines"

deserves to be widely known. He justly denounces it as "elandes Machwork"—a miserable counterfeit.

The main sections of the work treat of the technology of fuel, including lighting gas, the production of light, photometry, and the electric light; metallurgy in its widest sense; chemical manufacturing industry, including water, its examination, purification, and industrial applications; and thermo-chemistry—a subject which the industrialist can no longer safely overlook, since he may by its means learn if any proposed process is practicable or not. A peculiar interest attaches, of course, to the manufacture of soda and its by-products, which is now in a state of transition.

Section IV. treats of the organic chemical manufactures.

The chapters here devoted to the artificial colouring-matters and their examination are excellent, and go into practical details more than might be expected in work of such general scope.

The fifth section takes up glass, earthenware, cements, and mortars.

In the sixth we have an account of articles of food and consumption. The author's conclusions on the nutritive value of different kinds of food are instructive, though we fear the vegetarians will not be edified by learning that "meat, eggs, and milk are most completely utilised; vegetables much less thoroughly, as from 20 to 40 per cent are excreted undigested. A powerful body can scarcely be built up and maintained on a purely vegetable diet."

In the seventh section, we have the chemical treatment of fibres, including their cleansing, recognition, bleaching, dyeing, and printing; the manufacture of paper being naturally appended.

The last section is occupied with a somewhat promiscuous assortment of organic chemical arts and manufactures, tanning, glue, bone-black, fatty matters, soaps, stearine, and glycerin; the essential oils and resins; and the preservation of wood.

The editorial foot-notes in this edition are a most valuable feature. Many of them supply important facts overlooked in the original or discovered subsequently to the appearance of the last German edition. Very many are bibliographical, referring the reader to special works in which various subjects are treated more in detail than would have been possible in the work before us.

We are of opinion, however, that a treatise like the present, which gives a fair and accurate survey of the whole extent of chemical industry, is indispensable. With reference to the many special treatises which have lately appeared, it plays a part like that taken by a "key-map" in relation to the maps of provinces and cities. The various chemical arts throw cross-lights upon each other, often when least expected. Hence, to the rational industrialist, no less than to the student, this work will be invaluable.

Chemistry of the Carbon Compounds, or Organic Chemistry. By Prof. Von Richter, of the University of Breslau. Authorised translation by Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Second American Edition from the Sixth German Edition, with Illustrations. London: Kegan Paul, Trench, Trübner, and Co., Limited, 1891. 8vo., pp. 1040.

This book, though, according to its title page, it is published in London, has been written and printed in the United States, as may easily be seen from its peculiar orthography, and from a few expressions which are unusual on the eastern side of the Atlantic. The multitude of students, or, at least, of intending examinees, who busy themselves with chemistry, is an admitted fact. Still, the outsider is puzzled to account for the number of general chemical manuals of all sizes which are continually issuing from the press. How these works, the subject-matter of which is practically identical, find publishers is remarkable in times where original scientific productions meet with little acceptance, and is a question which has not yet found its Œdipus. Not content with the hand-books and manualettes of native origin we introduce English versions of German and French treatises, and now it seems American editions are making their appearance. All this is done in the absence of any discovery calculated to open up a new epoch in the history of Science. That the work before us is fully on a level with the present state of chemistry, that its views are correct, and its arrangement perspicuous, the name of Prof. von Richter is a full guarantee. No compound of importance is omitted, and although the descriptions are necessarily condensed they are accurate.

After an introduction, in which the general principles of organic chemistry are laid down, the two great classes of the fatty and the aromatic compounds and of the benzene—or as they are more commonly called aromatic—bodies are described. Lastly come certain compounds such as the alkaloids, the terpenes, the resins, &c., the constitutions of which have not yet been satisfactorily ascertained.

One feature is particularly satisfactory. The translator, not having the fear of any examiner before his eyes, has reproduced the work as he found it, without any alterations or additions supposed to be needful according to the requirements of the English or American student. There is no reference to preparing for any examination.

Experiments in General Chemistry. Systematically and progressively arranged. By Lyman C. Newell, A.M., Instructor in Physical Science, High School, Pawtucket, Rhode Island. Pawtucket: Sibley and Lee.

We have here a pamphlet of 23 pp. describing experiments to be made upon some thirty of the elements. The author gives the opinion that a careful performance of each experiment may not make a chemist, but it will make a sound thinker, and "to think is to live." This dictum is not unquestionable. Sometimes to think is to die. We notice the proviso as concerning the ignition of a mixture of hydrogen and air, "*perform this experiment with care.*" But will a *tyro*, perhaps without the presence of a teacher, know what kind of care is meant.

Elsewhere we read, anent the action of bleaching powder upon coloured tissues, "the chlorine destroys the organic matter in the cloth." Would it not be more accurate to say "destroys the colouring-matter in the cloth?"

Under hydrochloric acid the pupil is told to "cautiously touch a drop to the tongue;" and how is he to know the kind and amount of caution necessary? We think *with* the tongue would be a better expression. Several other passages in the pamphlet would be more intelligible if differently worded.

CORRESPONDENCE.

PAYMENT BY RESULTS.

To the Editor of the Chemical News.

Sir,—"Let it be granted that all teachers are thieves," postulated Parliament, and proceeded to elaborate a system whereby a thief might be set to catch a thief.

The effect of the system has been only too apparent to those who are capable of thinking straight and seeing clear, and Professor Humboldt Sexton has once more attempted to draw public attention to it in your issue of Jan. 15. But the public are past help in their blindness, for they *will* not see.

The result of regarding every teacher as a thief has been to compel him to become one. For what else can be said of him who sets aside all conscientious scruples

as to the utility of what he is teaching and the progress of his pupil, and converts himself into a machine for obtaining as much money from the public as the brains put under his charge will enable him to obtain? Yet such a course is the only alternative to starvation for him.

Now, Sir, there are at present being established in London several Institutions which are called and are to be called "Technical Institutes." These are supposed to be intended for the education of craftsmen in such sciences as may underlie the technique of their crafts—technical education no doubt expresses this, but has, unfortunately, become a shibboleth meaningless to many.

I submit, Sir, that these Institutions will one and all miss their mark if they be suffered to associate themselves with "the Department;" their teachers will at once be branded as thieves; and, lest they earn not enough grants for their employers, will neglect the unpromising craftsman for the smug board-school teacher, thus converting the so-called Technical Institutes into so many more night schools, of which there are at present plenty that turn out excellent "passes."—I am, &c.,

"ONE OF THE THIEVES."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 3, January 18, 1892.

Organic Compounds as Solvents of Salts.—A. Etard.—If the lines of the solubility of salts in water are beginning to be fairly well known it is not the same with other solvents. In a few cases a point of saline solubility in alcohol or ether has been determined, but the general progress of the phenomenon as a function of temperature still remains unknown for the various liquid media. Water, on account of its chemical and physical properties, is an exceptional solvent. It cannot be compared with any other, since it combines in various proportions with the majority of salts whilst still playing the part of a solvent. This double action renders the conclusions drawn from experiments very doubtful. The organic liquids rarely combine with salts. The anhydrous mercuric and cupric chlorides have, however, allowed of measurements which are summarised graphically in a subjoined table. Water dissolves sublimate between 0° and 120° along a curve, and from this temperature up to 150° the points lie in a right line. The experiments cannot be pushed very far above 150°, the salt is dissociated and chlorine is liberated in the liquid. The solutions, which up to 120° deposit on cooling the well-known needles of anhydrous mercuric chloride give above this temperature white nacreous tablets resembling in form mercuric iodide. Absolute methylic alcohol approaches very near to water. It is water in which a hydrogen has been replaced by a carbide radicle very near to CH_3. Absolute ethylic alcohol presents a double perturbation between $-50°$ and $+60°$. In the organic liquids, as in water, mercuric chloride is deposited from hot solutions in tablets. Both with the organic liquids and with water we may observe right lines of solubility directed towards its fusion point. This fact, the demonstration of which the author intends to pursue, will establish for salts a direct connection between the gaseous state and the state of solution.

Action of Carbon Monoxide upon Iron and Manganese.—M. Guntz.—In the author's experiments it appeared that at dark redness iron seemed to absorb carbon monoxide, whilst it was blackened by a deposit of carbon; carbonic acid was also evolved, though in small quantities. Pure manganese absorbed the carbon monoxide, producing even a partial vacuum in the apparatus. This gas is dissolved according to the formula—

$$Mn+CO=MnO+C.$$

At very high temperatures manganous and ferrous oxides, if heated with carbon, yield metal and carbon monoxide, the inverse reaction of that which takes place about 500°.

Action of Carbon upon Sodium Sulphate in Presence of Silica.—Scheurer Kestner.—It is generally admitted that the reactions effected between the alkaline sulphates, carbon, and silica, in the production of glass or of soluble silicates, are represented by the equation $2RSO_4+C=2SO_2+CO_2+2RO$. If the proportion of carbon is insufficient the glass is incomplete and contains an alkaline sulphate; if it is too large the glass is sulphurous, and its solution, in case of sodium silicate, blackens lead salts. But the necessary quantity of carbon considerably exceeds that which answers to the above equation. From the author's experiments he concludes that the sulphur of the sodium sulphate is entirely given off as a vapour mixed with much carbon dioxide and a smaller quantity of carbon monoxide. Even in presence of a large excess of sulphate the proportion of carbon monoxide remains important, and forms the sixth part by volume of the total gas produced. It is probable that this carbon monoxide is derived from a decomposition giving rise to sulphurous acid, which is in turn decomposed at higher temperatures by the carbon. The formation of sodium silicate takes place thus—

$$3SO_4Na_2+6SiO_2+5C=3S+4CO_2+CO+3(Na_2O.2SiO_2).$$

On a Lithium Nitride.—L. Ourard.—Lithium heated in a current of nitrogen contained:—

Lithium (total)	54·18
Nitrogen	35·86
Silica	6·84
Oxygen	3·12
	100·00

Of the lithium 2·73 was combined with oxygen and 51·45 with nitrogen. The compound produced seems to be NLi_3.

Action of Phosphorus Perchloride upon Ethyl Oxalate.—A. Feuconnier.—By the reaction of the two constituents the author obtains oxalyl chloride, and on heating 2 mols. phosphorus perchloride and 1 mol. ethyl oxalate, he produces a mixture of ethyl and oxalyl chlorides and phosphorus oxychloride. Oxalyl chloride is a colourless, mobile liquid, fuming strongly in the air. It is decomposed in contact with water, yielding oxalic acid.

The Value of the Two Functions of Glycol.—M. de Forcrand.—Not adapted for useful abridgment.

An Isomer of Camphor.—Ph. Barbeir.—This new isomer of camphor, to which the author gives the name puleone, exists in the essential oil of *Mentha pulegium*. Its composition is $C_{10}H_{16}O$. It is colourless, very mobile, with a strong odour of mint; it is insoluble in water, soluble in alcohol, ether, and benzene. It boils at 222°—223°. Its specific gravities at 0° and 23° are 0·9482 and 0·9293. It is dextrorotatory, and its rotatory power for the ray D is $[\alpha]_D = -25·15°$. The indices of refraction with relation to two rays of tin are—

$n_\gamma = 1·4833$	$\lambda_\gamma = 645$
$n_b = 1·4997$	$\lambda_b = 452·6$

Puleone contains the functional group of the ketones. It does not contain ethylenic groups.

Fixation of Iodine by Starch.—E. Rouvier.—There is formed in presence of an excess of starch a compound different from that formed in presence of an excess of iodide.

Action of Boric Acid upon Germination.—J. Moret.—It may be concluded that boric acid in solution, if placed in contact with the seeds of plants, retards and even prevents germination if the contact is sufficiently

prolonged. Boric acid will probably act strongly upon the lower fungi and kindred organisms. If this is the case boric acid may be employed in combating mildew, *anthracnose*, *oideum*, &c.

Rotatory Power of Silks of Different Origin.—Leo Vignon.—The molecular rotatory powers measured have all the same sign. For the gum they are comprised between $-30°$ and $-45°$, and for the fibroines between $-39·5°$ and $-48·2°$.

Sodium Chloride in Plants.—Pierre Lesage.—On watering *Lepidium sativum* and *Raphanus sativus* with dilute sea-water or dilute brine, we find in the plants the elements of this salt, which are therefore absorbed in a certain proportion.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 11.

The Conditions which should be Presented by Fermentible Solutions in order that Fluorides may Produce in them a Maximum Effect.—J. Effront.—The experiments recently undertaken by the author prove that the beneficial action of the fluorides depends on a number of conditions. The acidity of the wort especially regulates the antiseptic action; in a neutral wort it is nearly null, but increases with the acidity. The acidity plays a very important part in the special action of the fluorides upon the protoplasm of the cellules, but the presence or absence of phosphates constitutes one of the most important conditions of the activity of the phosphates.

Preparation of Zinc-Hydroxylamine.—L. Crismer.—On account of a memoir recently published by M. Lobry de Bruyn, the author is compelled to make known two very simple procedures for the preparation of crystalline hydroxylamine, which depend on the use of the zinc salt.

Preparation of Crotonic Aldehyd.—A. Müller.—The best yield is obtained by heating for forty-eight hours 100 grms. of absolute ethylic aldehyd with 0·7 c.c. of a solution of zinc chloride containing 150 grms. of this salt in 100 c.c.

The Presence of an Aldehyd with Four Atoms of Carbon in a Piquette Brandy.—J. A. Müller.—The author finds it remarkable to meet in a brandy with a relatively considerable quantity of an aldehyd having a definite composition.

Action of Sulphur upon Metallic Solutions.—J. B. Senderens.—The author describes first the action of sulphur upon the alkaline and alkaline-earthy bases; next the action of sulphur upon the metallic oxides in presence of water; thirdly, the action of sulphur upon salts in presence of water, taking in succession the sulphates, nitrates, and chlorides, the acetates, the carbonates, the silicates, including glass and various polybasic salts. He treats lastly of the action of sulphur upon water. He maintains that under these conditions the production of hydrogen sulphide affirmed by De Gerard, denied by Gélis, and re-affirmed by Cross and Higgin, is very slight.

Action of Light upon Silver Chloride.—A. Béchamp.—Already noticed.

MISCELLANEOUS.

Royal Institution.— Professor E. Ray Lankester, F.R.S., will, on Thursday next, February 11, begin a Course of three Lectures on "Recent Biological Discoveries"; and the Right Hon. Lord Rayleigh, F.R.S., will, on Saturday, February 13, begin a Course of six Lectures on "Matter, at Rest and in Motion."

The Royal Society of New South Wales.—*Original Researches.*— The Royal Society of New South Wales offers its Medal and £25 for the best communication (provided it be of sufficient merit) containing the results of original research or observation upon each of the following subjects:—

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MEETINGS FOR THE WEEK.

Monday, 8th.—Medical, 8.30.
— Society of Arts, 8. "Developments of Electrical Distribution," by Prof. George Forbes, F.R.S.
Tuesday, 9th — Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8. (Anniversary).
Wednesday, 10th.—Society of Arts, 8. "Burning Oils for Lighthouses and Lightships," by E. Price Edwards.
— Geological, 8.
— Pharmaceutical, 8.
Thursday, 11th.—Royal, 4.30.
— Royal Institution, 3. "Some Recent Biological Discoveries," by Prof. E. Ray Lankester, M.A.
— Society of Arts, 4.30. "Recent Travels in Indo-China," by Lord Lamington.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
Friday, 12th.—Royal Institution, 9. "On Rain, Snow, and Hail," by G. J. Symons, F.R.S.
— Astronomical, 3. (Anniversary).
— Physical, 5.
Saturday, 13th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

TO CORRESPONDENTS.

E. Toray.—As you put it we do not see how it is possible.

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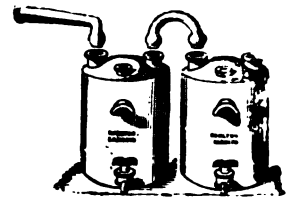

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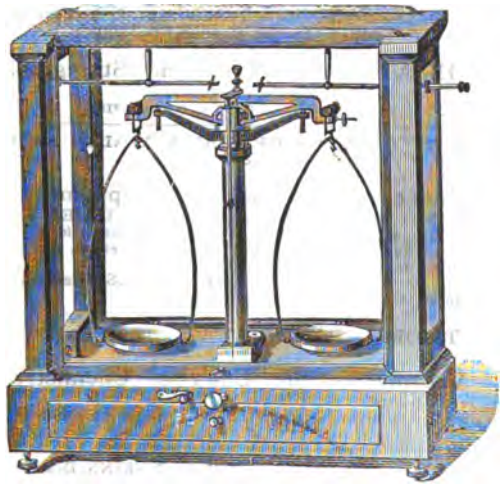

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Vol. LXV., No. 1681.

THE ALDE-ACIDS.

By J. ALFRED WANKLYN and WILLIAM JOHNSON.

Valerianic Acid.—There are four possible valerianic acids, viz., the normal acid and three iso-acids; and, consequently, there are three possible alde-valerianic acids. There is an acid which has been known to chemists for forty years under the name of angelic acid, $C_5H_8O_2$. It is a crystalline solid, fusing at 45·6°, and volatile, boiling at 190·6°. We expect to find that this acid is one of the four possible alde-valerianic acids, and we call attention to the fact recorded in "Watts's Dictionary," that valerianic acid when oxidised by alkaline permanganate yields a crystalline acid, supposed to be angelic acid.

We have operated upon commercial valerianic acid with alkaline permanganate and obtained a crystalline acid which we intend to investigate.

Ascending the series, we have experimented upon palmitic acid and margaric acid. The specimen of palmitic acid was prepared from palm oil and carefully and laboriously purified. Its baryta salt was found to contain 20·92 per cent of barium. Some of this was oxidised by alkaline permanganate and converted into a different acid, which furnished a baryta salt containing 21·31 per cent of barium. Theory for alde-palmitate of baryta—barium 21·31 per cent.

The margaric acid was that which in commerce passes under the name of stearic acid. Operating upon this acid we have shown that when gently heated in the water-bath in presence of alkaline permanganate and much water, it is attacked and converted into a new acid possessing very marked properties. There appears to be no—or next to no—utter destruction. In our experiment, 2·34 grms. $C_{17}H_{34}O_2$ reduced 0·880 grm. $KMnO_4$ to the state of H_2OMnO_2, and yielded 2·25 grms. of the new alde-margaric acid; the formula of which we expect will be $C_{17}H_{32}O_2$.

We are engaged in an extended investigation of the new acids and believe we have in our hands the following members of the alde-acid series:—

$C_{17}H_{32}O_2$,
$C_{16}H_{30}O_2$,
$C_5H_8O_2$.
$C_4H_6O_2$.

There is a strong family likeness running through them, and some of them are destined to become important in many ways.

ON THE EXPLOSION OF SODIUM BOTTLES.

By Dr. T. L. PHIPSON, F.C.S., &c.

A recent number of the Chemical News (vol. lxv., p. 61) contains a letter from Mr. A. Merry, of Swansea, which gives an account of the explosion of a bottle containing sodium which had stood unused in a laboratory *for two years*, the petroleum which covered the metal having, it is supposed, been evaporated so as to leave the metal in contact with the air. The writer of the letter demands an explanation of the phenomenon.

I have two bottles of sodium prepared by Henri Ste.-Claire Deville, in Paris, about the year 1858. I brought them to London with me in 1860, and they have thus been for *upwards of thirty years* on the shelves of my laboratory. They are stoppered glass bottles. One of them has been frequently opened, and its supply of sodium is now reduced to about one-quarter of what it originally was. The other has been used less frequently and is still nearly full. From time to time the petroleum which covers the metal has been added to, in order to supply the loss that occurs by slow evaporation, in spite of the excellent glass stoppers. But of late years this evaporation by the stoppers has entirely ceased; a thin air-tight film of some petroleum compound having formed over the surface of the stoppers; and since 1880, or thereabouts, it has been necessary to take out the latter now and then, for a moment, when the bottles have not been in use for a long time, otherwise their extraction is exceedingly difficult, on account of a certain amount of vacuum produced between the surface of the petroleum and the stopper. This result is due to an absorption of oxygen by the sodium. It is evident, from many observations I have made, that this metal will draw oxygen from the air in the upper part of the bottle in spite of the naphtha, and in the course of a few months the partial vacuum thus produced can be appreciated by the marked resistance of the stopper to leave the neck of the bottle, though it can easily be turned round. It may be that sodium would deoxidise a resinified petroleum, and the deoxidised resinous matter, in its turn, absorb oxygen from the air of the bottle. Anyhow, a partial vacuum is produced, which, in the case of a large, thin, or defective glass bottle, might give rise to an explosion by external atmospheric pressure. But in the Swansea explosion it appears more probable that water or acid has had access to the metal after or during the evaporation of the naphtha, since some of the fragments of the metal strewn about were ignited; and the origin of this water or acid will have to be sought for. Petroleum is lighter than water and floats readily on the surface, but the oil can be mixed with a small quantity of water, and like many vegetable oils may be damp. The presence of even a small amount of water or acid would be sufficient to account for the accident; and the question arises—whether water or some organic acid may not be formed from impure resinified petroleum by the prolonged deoxidising action of sodium? and, whether any sulphuric acid used in purifying the naphtha may, in this case, have remained in it? The latter seems to me the most probable.

Not being acquainted with all the facts which surrounded the bottle of sodium at Swansea, and the possible impurities of its contents, I cannot, of course, enter into any more minute explanation of the extraordinary result recorded in the letter referred to above. We require more details.

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THE DETERMINATION OF COBALT IN MANGANESE ORES, AND A QUICK METHOD FOR ITS ESTIMATION.

By THOMAS MOORE.

The assay of the ores in question is one which, if not exactly presenting any great difficulty, is, nevertheless, exceedingly tedious, usually inconveniently long, and requires almost undivided attention throughout its entire course. At first sight there would appear to be no trouble in separating the iron and alumina from the cobalt, nickel, and manganese by treatment with ammonia hydrate or by sodic acetate, but a very short experience will suffice to demonstrate that the former is absolutely worthless, and that the basic acetates of the latter must be precipitated at least four times before one can be assured that the separation, as far as the cobalt is concerned, is sufficiently complete. The filtration, too, of these slimy precipitates requires the utmost patience, and the large bulk which

the filtrate too often assumes all tend to the consumption of much time.

The two methods which I give have been devised to avoid, or at least diminish, these inconveniences. The first process, although bearing no comparison to the second for rapidity, can be confidently relied upon to furnish rigorously exact results for a minimum expenditure of time, gives also easily filtered precipitates and filtrates of reasonable volumes. The second method, which I believe is quite new, gives results quite accurate enough for all technical purposes, and by paying careful attention to all sources of error will furnish figures which, for all practical purposes, are exact; but its great recommendation is that an hour is ample time for the complete operation.

First Method.—Two grms. of the ore are fused in a platinum basin for fifteen or twenty minutes with 4 or 5 grms. potassic bisulphate at the highest temperature a Bunsen burner is capable of giving. At the end of this time the mixture will be in a quiet state of fusion; remove the cover and (still continuing the heating) add a piece of ammonic carbonate about the size of a pea, replace the lid, so as to avoid loss by spirting, and repeat the addition of the carbonate until the mass evolves the fumes of SO_3 but feebly, then pour the melt upon a clean slab of metal and allow to cool. About 400 c.c. of water are now raised to the boiling-point in a beaker of glass and the rose-coloured melt, together with the rinsings from the crucible, carefully added. The solution is then boiled for twenty minutes so as to ensure complete solution of all soluble matter. The insoluble residue is now allowed to settle, the clear liquid passed through a filter, and the insoluble matter, after being repeatedly boiled up with successive portions of water, is thrown on a filter and well washed with boiling water. The precipitate of silica and basic sulphates will be found on testing to be quite free from either cobalt or nickel and filters with the greatest facility. The filtrate is now heated, 30 c.c. acetic acid added, and a rapid stream of sulphuretted hydrogen passed through it; as soon as the small quantity of iron still remaining in the solution appears to be reduced, add about 50 c.c. of a strong solution of ammonic acetate, when, if the solution has been kept boiling, all the cobalt and nickel will be precipitated. The sulphides so precipitated settle readily to the bottom of the flask, are very dense and compact, and much less liable to oxidation than when thrown down in the usual manner from cold solutions. After having been well washed, the precipitate is dried and then calcined at as low a temperature as is compatible with the thorough destruction of the filter paper, then dissolved in a few c.c. hydrochloric acid and converted into sulphates by evaporation with sulphuric acid. From the solution of the sulphate so obtained the two metals are electrolytically deposited in the usual manner after the addition of an excess of ammonic hydrate; the small amount of peroxide of iron usually present floats in the solution and has no appreciable influence on the results. Having determined the joint weight of the two metals, they are then dissolved off the cone and their further evaporation carried out by any of the well known processes, the precipitation of the cobalt as the ammonic phosphate being the most suitable.

Second Method.—This method admits of cobalt being directly determined in the presence of a large number of bodies, some of which present considerable difficulties by the usual modes of separation. The principle upon which it depends is that of the absorption of oxygen by ammoniacal solutions of cobalt; this absorption, when cobalt alone is present, is very energetic and complete, likewise in the resence of nickel or other salts which form soluble compounds with ammonia. Manganese, like cobalt, forms a double salt with ammonia, and this, too, on exposure to air absorbs oxygen. If, however, we take a solution of the two metals containing an excess of citric acid, then on adding ammonia it will be found that though the cobalt absorbs oxygen somewhat less energetically than before, the manganese has this property so much enfeebled that the amount absorbed during the experiment is so small as to be negligible; the addition of citric acid having the effect of causing an ammoniacal solution of manganese to become practically indifferent to air. Taking, then, this fact into consideration, and remembering that citric acid effectually prevents the precipitation of iron or aluminium solutions by ammonia, it is easy to see how this can be applied for the cobalt assay by simply measuring the volume of oxygen absorbed; thus, leaving the ammonia out of the question, the formula is—

$$2CoO + O = Co_2O_3.$$

That this Co_2O_3 may be united to various proportions of NH_3, forming different cobaltamines, does not affect the case, their formation being a matter of no moment so long as the total oxygen absorbed remains constant. There is therefore required for the oxidation of 118 grms. of cobalt 11,200 c.c. of oxygen at 0° C. and 760 m.m. pressure. Hence, for every c.c. (at the standard temperature and pressure) of oxygen absorbed there is 0·0105 of Co required.

Two grms. of the ore are taken for the assay and evaporated to dryness with hydrochloric acid; to the residue 3 grms. of citric acid dissolved in 3 or 4 c.c. of ammonia are added, care being taken that the acid is in slight excess; if alkaline, a drop or two of HCl must be added so as to obtain a *distinct* acid reaction. The residue and citric acid solution are now heated until all soluble matter is dissolved; 2 or 3 c.c. water may be added if too concentrated, and then allowed to cool. The solution is then transferred to the apparatus figured in the sketch, and the volume made up to the zero mark with water. A sufficiency of the strongest liquor ammonia saturated with ammonic chloride is now injected in the usual manner with the Bunte gas burette, of which it will be noticed this is simply a modification, or a given volume of air may be withdrawn by placing a second burette filled with water alongside, and connecting the two by a piece of rubber tubing provided with a clip and filled with water, care being taken to exclude air bubbles, and allowing a portion of the water in the second to flow away; the requisite amount of ammonia (4 or 5 c.c.) can now be passed into the first burette by opening the lower tap. It is unnecessary to occupy space by going into further details, as the manipulation is in every respect similar to that of the well

known aforesaid burette. The apparatus is now well and violently shaken until all absorption ceases, which can be known by placing the lower orifice in a little ammonia and noting if the latter continues to enter the bulb on opening the tap. The ammoniacal liquid is now thoroughly displaced by a current of pure water, entering by the upper and passing away by the lower outlet, and if the duplicate burette has been employed the air abstracted must be transferred to the original by connecting as before and passing a current of water through both apparatus, entering by the lower tap of the second and passing away by the lower tap of the first. Having allowed the apparatus to attain a uniform temperature, the pressure of the enclosed gas is now corrected and brought, by any of the usual methods, to that of the atmosphere. There now only remains to be done the reduction of the volume of oxygen absorbed to the standard temperature and pressure, taking into account the tension of the water vapour, either by the formula—

$$Vo = \frac{V\,273\,(B-f)}{(273+t)\,760}$$

or by the very convenient piece of apparatus first proposed by Williamson and Russel, and fully described in "Winckler's Quantitative Gas Analysis," page 35, German edition.

Too much attention cannot be paid to the taps; they must be perfectly air tight and frequently paraffined, as the leakages caused by them when badly fitted give rise to errors extremely difficult to detect. The apparatus should be placed in a tank of water for at least five minutes before taking measurements, so as to ensure a uniform temperature, and the solution must be thoroughly washed out of the burette first with pure water and then with a weak solution of some acid, to absorb any ammoniacal gas.

It should, perhaps, be mentioned that although the silica present in the ore is, of course, without influence upon the results, still it is better to filter it off, as the fine particles getting entangled in the glass tap soon render it useless. As already mentioned, the method leaves scarcely anything to be desired in the presence of nickel or other compounds forming soluble salts with ammonia, the oxidation being prompt and complete. With the employment of citric acid, the only difference is that the absorption is more gradual, and as the greater part of the cobalt becomes oxidised, the absorption becomes still slower; never, however, as far as my experience has gone, to such an extent as to exceed the time mentioned. Iron, it is hardly necessary to state, must, if present, be first converted into the ferric state.

New Caledonia, December 12, 1891.

CONTRIBUTIONS TO CELLULOSE CHEMISTRY.

By C. F. CROSS and E. J. BEVAN.

THIS subject continues to attract investigators, and the past year has been distinguished by important communications, notably those of Tollens and his fellow workers, E. Schulze and W. Will (*Berl. Ber.*, 1891, 400, 694, 2277, 3575). In view of the rapid convergence of the lines of research followed by the workers in this field, we take the opportunity of recording a few brief notes of results obtained by ourselves, in anticipation of their fuller treatment, which we reserve until they may be regarded as completing a chapter in the development of the subject.

Cellulose Benzoates.—The hydrates of cellulose (cotton) obtained by precipitation from its solution in the ammonio-cupric reagent or in $ZnCl_2.HCl$ (CHEMICAL NEWS, lxiii., p. 66), are completely dissolved by solutions of the alkaline hydrates.

These solutions shaken with benzoyl chlorides, according to Baumann's method, yield a white curdy precipitate of a benzoate. After purification by solution in glacial acetic acid, &c., it yields on analysis numbers corresponding with the formula of a *dibenzoate*—

$$C_6H_8O_3(C_7H_5O_2)_2.$$

This benzoate is soluble in acetic anhydride, and on boiling the solution with the addition of fused sodium acetate, a product is obtained which appears to be the triacetyl monobenzoate.

When cellulose is treated with a strong solution of sodium hydrate (15 per cent Na_2O), and the mixture of "mercerised" fibre and alkali shaken with benzoyl chloride, combination takes place, there is an increase of weight of 60—70 per cent, and the purified product yields on analysis numbers corresponding with the formula of a *monobenzoate*.

It appears, therefore,—retaining for the moment the C_6* formula for cellulose—that of the five O-atoms four are capable of reacting as OH; that in the solution of the hydrate of cellulose in alkaline hydrate, two of the OH groups react with the alkali, which two are benzoated by reaction with the anhydrochloride, and that in the "mercerising" action of the alkaline hydrates one OH group only is brought into play. We now have, in the benzoates, acetates, acetobenzoate, and nitrates of cellulose, a fair range of ethereal derivatives which we have every reason to regard as simply related to the parent molecule. We have next to determine such physical constants for these derivatives as shall afford criteria of molecular weight and volume, and in this way to arrive at an approximate estimate of the reacting unit, or the molecule of cellulose.

Cellulose Terminology.—The researches of Schulze and others (*Berl. Ber., loc. cit.*), chiefly upon the constituents of seed-tissues, have brought to light a variety of forms of cellulose, various in regard to the simpler carbohydrates into which they are resolved by hydrolysis, and of which, therefore, they may be regarded as the anhydro-aggregates. In addition to those which yield dextrose, there have now been brought to our knowledge cellulosic forms of mannose, galactose, arabinose, &c.

Some years ago we ourselves called attention to the fact that the celluloses of the Gramineæ are differentiated by a characteristic colour reaction (rose-red) on boiling with solution of aniline sulphate, and by yielding furfural on hydrolysis. Schulze has isolated a number of celluloses yielding this aldehyd on hydrolysis, of which he has also determined the yield (*Berl. Ber.*, 1890, 2284).

The formation of furfural we now refer, on the basis of the researches of Tollens, to a pentaglucose molecule, a constituent of the celluloses in question. We ourselves usually observe that this aldehyd is accompanied by acetic acid in the distillate,†—an observation which, we think, should be followed up with a view to a possible further light on the mechanism of the hydrolysis. It is noteworthy that both furfural and acetic acid have the ratio $C_mH_{2n}O_n$, and their formation from any carbohydrate therefore involves empirically only a + or − of H_2O molecules.

It is, perhaps, premature to adopt as final any of the proposed additions to the terminology of this wide group of plant constituents. We can only retain the original term cellulose as the substantive or group designation, and leave the adjectives to the struggle for survival.

Hydrolysis of Cellulose.—The remarkable results which have been obtained of late years from the study of the hydrolytic dissection of the starch molecule clearly indicate that for anything like a complete study of the molecular structure of the celluloses they must be subjected to a similar process of disintegration into known products. The study of the ethereal derivatives which we have been prosecuting is the exact converse of this; but while, however, it is not to be accorded precedence on first

* We propose, for reasons given (*infra*), to abandon the nC_6 for the nC_{12} formula for (cotton) cellulose.

† From pure straw (oat) cellulose, by solution in H_2SO_4 in the cold, diluting and distilling, we have obtained 4—10 per cent of its weight of $C_nH_4O_m$ together with 3—5 per cent furfural.

principles, we are of opinion that valuable results are to be obtained by studying cellulose as a molecular aggregate. In the meantime, Messrs. Brown and Morris are making progress in the study of the "cytohydrolytic" ferment of the barley corn, and to them and others who are in the position of attacking the cellulose problem from the bio-chemical point of view we must look for light in this direction. The hydrolytic processes of the laboratory can hardly be expected to do more than reveal the nature of the ultimate constituent groups, *i.e.*, the simpler carbohydrates of which the celluloses are built up; and the more drastic decompositions, such as that brought to light by W. Will, who obtains hydroxypyruvic acid—

$$CH_2OH.CO.COOH,$$

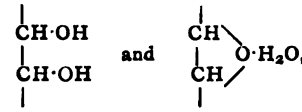
as a product of the resolution of cellulose nitrates by dilute alkaline solutions, are of course still less likely to show how the constituent groups are put together, although they cannot fail, of course, to throw valuable light upon their constitution.

Failing, therefore, in the meantime, any "natural" hydrolytic agent available for isolation and control to suit the exigencies of the laboratory, we can only continue in the two directions of study (*a*) of synthetical derivatives of simple relationship to the original molecule, and (*b*) of products of what we may term wholesale hydrolysis.

Constitution of the Celluloses.—It is obvious that for the present we must be content with general conclusions as to the constituent groups of the celluloses, and a suspension of judgment as to how they are put together. For the typical cotton cellulose the balance of evidence would lead us to adopt a C_{12} formula for the unit group, of which we may assume it to be the anhydro-aggregate.

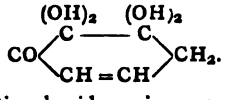
The main points in the evidence are the relationships of this cellulose to starch and the conclusions drawn from the study of the nitrates.* Of the ten oxygen atoms in such a formula, eight appear to be capable of reacting as OH oxygen. The two remaining there is every ground for regarding as in the form of carbonyl oxygen. In support of this we may cite (1) the formation of hydroxypyruvic acid as a product of resolution of the nitrates by dilute alkaline solutions in the cold (W. Will). (2) Our own observations, hitherto unpublished, of the formation of large quantities of acetic acid (10—20 per cent), by fusion of cellulose with alkaline hydrates at 300—400°; (3) the aldehydic and ketonic character of the products of resolution by simple hydrolytic processes.

The differentiation of the OH groups would be accounted for by proximity to a CO or a CH_2 group in the molecule; and the fact that the OH groups, at least in cotton cellulose, are latent rather than active, would be explained by assuming that in cellulose we have steps intermediate between—



such as we are familiar with in the hydrates of the inorganic oxides, water of crystallisation, &c.

Lignocelluloses.—The characteristic reactions of the lignocelluloses, typified by the jute fibre, we have referred to the presence of groups of the general form—



We have additional evidence in support of this view in a recent observation, that when jute is dissolved in the $ZnCl_2.HCl$ reagent and the solution treated with bromine, there is direct combination in the cold with the halogen. The quantity entering into combination being, moreover, one-half (the equivalent of) the chlorine combining with the fibre substance to form the characteristic quinone chloride (*Chem. Soc. Journ.*, vol. lv., 200).

In addition to these groups which appear to be condensed into complexes of C_{18}, *i.e.*, three C_6 groups, we have what we may term the cellulosic basis of the fibre, a cellulose which, when isolated, is found to resemble very closely the normal cotton and linen celluloses, the proportion of this being from 75—80 per cent of the raw fibre. This cellulose we may term cellulose *α*. The third constituent we had identified, at the time of publishing our last paper (*Chem. Soc. Journ.*, 1889, 200), as a carbohydrate yielding furfural and acetic acid as products of hydrolysis. By the action of chromic acid in presence of dilute acids in the cold we have succeeded in oxidising away the quinone constituent, leaving the carbohydrate in question in the form of a cellulose associated with the before mentioned cellulose *α*. We find that the yield of acetic acid (and furfural) is unaffected by the treatment, and the identification of this third constituent, or cellulose *β*, is therefore complete. The jute fibre, therefore, may be regarded as an anhydro-aggregate of:—

Cellulose α—Probably a dextroso-cellulose allied to cotton and linen cellulose.

Cellulose β—A penta-cellulose yielding furfural and acetic acid on hydrolysis.

Lignone—A C_{18} quinone or quinol converted by chlorination and reduction into derivations of the trihydric phenols.

We submit the above brief notes of results of current work, pending their completion and confirmation for an exhaustive communication to be submitted in due course to the Chemical Society, from whose Research Fund we have been fortunate in again receiving a substantial award.

* We obtain from "soluble" starch treated by Baumann's method a benzoate similar to that from cellulose, and giving analytical numbers corresponding with a tetrabenzoate (C_{19}) formula.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

(Continued from p. 69).

THIS method may be expanded, as proposed by Mr. McElroy, so as to permit the estimation of other bases in the same portion of the material. For this purpose the filtrate and washings from the first precipitation are collected. Sufficient ammonium oxalate is added to them to precipitate the calcium. As the ammoniacal solution must be kept cool, this precipitate is very fine, and I have found that the only way to collect it satisfactorily is by using a Gooch crucible without pressure. By proper packing of the asbestos film, the filtration can be made quite rapid and satisfactory. The filtrate and washings are again collected, and a solution of sodium phosphate added to precipitate the magnesia. It is absolutely necessary to keep all solutions cold and ammoniacal during these operations, so as to prevent the separation of molybdic anhydride.

Of the methods lately proposed for the determination of iron and aluminium in phosphates the most prominent is the method of Glaser, also called the "alcohol method" (CHEMICAL NEWS, lxiii., p. 146).

Glaser proceeds as follows:—

5 grms. of the phosphate are dissolved in the usual manner in 25 c.c. nitric acid (specific gravity 1·20) and 12·5 c.c. of hydrochloric acid (specific gravity 1·20) and made up to 500 c.c. 100 c.c. of the filtrate are placed in a 250 c.c. flask with the addition of 25 c.c. of sulphuric acid (specific gravity 1·84). The flask is allowed to stand for five minutes, shaking occasionally. About 100 c.c.

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 12.

of 95 per cent alcohol are added, the flask is cooled, made up to the mark with alcohol, and well shaken. After standing half an hour the liquid is filtered. 100 c.c. of the filtrate (=0·4 grm.) are evaporated down in a platinum capsule until the alcohol is expelled. The residual solution is mixed with 50 c.c. water in a beaker and brought to a boil. Ammonia is then added to the solution until the reaction is alkaline, but not whilst boiling, to avoid violent effervescence. The excess of ammonia is removed by boiling, the solution is allowed to cool, filtered, the precipitate washed with hot water, ignited, and weighed as ferric and aluminic phosphates.

Jones (*Zeit. fur Angew. Chemie*, 1891, No. 1, p. 3) investigated Glaser's method and found that—

(*a*) The amount of alcohol prescribed was not sufficient to precipitate all the calcium sulphate.

(*b*) The amount of sulphuric acid is much more than is actually necessary.

He therefore modified the method as follows:—

10 grms. of the substance are dissolved in nitro-hydrochloric acid, and the solution made up to 500 c.c. 50 c.c. of this solution (= 1·0 grm.) are evaporated down to 25 c.c., and, whilst hot, 10 c.c. of dilute sulphuric acid (1 : 5) added, the whole stirred and cooled. 150 c.c. of 95 per cent alcohol are then added, and after stirring, the solution is allowed to stand three hours. The calcium sulphate is then collected on a filter, washed with alcohol, and the filtrate and washings collected in an Erlenmeyer flask. The washing is complete when the last ten drops, after dilution with an equal volume of water, are not coloured red with a drop of methyl-orange.

The calcium sulphate, whilst moist, is transferred to a platinum crucible, the filter placed on it, the alcohol burnt off, and the filter incinerated. The calcium sulphate is then ignited and weighed. The contents of the flask are heated to expel the alcohol, the residue washed into a beaker, made slightly alkaline with ammonia, and again heated until all the ammonia is driven off. This is absolutely necessary, as otherwise the precipitate will be contaminated with magnesia. The precipitate is collected on a filter, washed four times with hot water or water containing ammonium nitrate, dried, ignited, and weighed.

An excess of ammonia is added to the filtrate and washings, the whole allowed to stand twelve hours, when the magnesia will have separated as ammonium-magnesium phosphate, which can be collected, ignited, and weighed as usual.

Immediately after the above methods were published, considerable discussion arose with regard to the presence of magnesia in the precipitate of iron and aluminium phosphates.

Theodor Meyer (*Zeit. fur Angew. Chemie*, 1891, viii., p. 243) states that unless all of the ammonia is driven off the precipitate will contain magnesia, and, on the other hand, continued boiling not only drives off the free ammonia, but also some of the combined, forming acid ammonium sulphate, which re-dissolves some of the precipitate. This, however, separates out again on standing.

K. Wohlrab (*ibidem*, 1891, p. 170) and von Gruber (*Zeit. fur Anal. Chem.*, xxx., pp. 206, 207), however, dispute Meyer's statement, reporting analyses of known mixtures.

It does seem improbable that during the short time which is required for the precipitation any appreciable quantities of magnesia could separate.

(To be continued.)

Action of Chlorine upon Certain Acetones of the Fatty Series.—Demetrius Vladesco.—This memoir, too lengthy for insertion, is the last portion of an investigation which has been interrupted by the death of the author.—*Bull. de la Soc. Chim. de Paris* vi., No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

January 21st, 1892.

Professor W. A. Tilden, F.R.S., Vice-President, in the Chair.

Messrs. L. W. Fulcher, Harry G. Myers, Ph.D., and Thomas Stephenson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Fielding Bond, M.D., Rastrick, Yorks; William John Atkinson Butterfield, 10, Tressillian Crescent, St. John's, S.E.; Robert Brooke Floris, 18, Ridgway Place, Wimbledon, S.W.; Alfred Thomas Gailleton, Tulloch House, Perth, N.B.; William Percy Hatton, 73, St. Quintin Avenue, North Kensington; Lionel Manfred Jones, Beaumont House, Llanelly; William Cossar Mackenzie, Tewfikieh College of Agriculture, Ghizeh, Cairo; Charles Stephen Meacham, 62, Earl Street, Maidstone; Thomas Skurray, Abingdon, Berkshire; James Sykes, 76, Lockwood Road, Huddersfield.

Of the following papers those marked * were read:—

*93. "*The Estimation of Oxygen Dissolved in Water.*" By Matthew A. Adams.

The author describes an apparatus in which the estimation of oxygen in water by Schützenberger's method may be carried out so as entirely to avoid the loss of oxygen by diffusion or its entry. The essential feature is a cylindrical laboratory vessel about 350 c.c. in capacity, 20 c.m. long, and 5 c.m. in diameter, provided with four small lateral tubulures midway from the closed ends. By means of these it is attached to two burettes, one containing the indigo carmine, the other hyposulphite solution, and also to a mercury reservoir and to a Y-tube, one branch of which is connected with a supply of the water to be examined, the other serving as an outlet for the water. The tubes are all controlled by pinchcocks. The water and the liquids for titration are sucked into the vessel by lowering the mercury reservoir, and are subsequently discharged by raising it again; the tubes passing into the vessel from the burettes are provided with india-rubber valves which prevent either reflux or diffusion taking place into the burettes.

The author then refers to the peculiar irregular manner in which the action is known to take place, and describes his own observations, giving the results both of experiments made in the manner directed by Schützenberger and in the indirect manner recommended by Roscoe and Lunt (*cf. C. S. Trans.*, 1889, 552). From the results he concludes that in estimating oxygen by the Schützenberger process, the result obtained is liable to differ according to the rate at which the determination is effected, it being always higher when the titration is quickly performed.

*94. "*The Luminosity of Coal-gas Flames.*" By Vivian B. Lewes.

The author has quantitatively studied the actions which lead to loss of luminosity in a Bunsen flame.

The volumes of varying mixtures of nitrogen and oxygen required to render 16·3 candle coal-gas non-luminous in a Bunsen burner are shown in the following table:—

Gas.	Volume of mixture required.	Composition of mixture. Nitrogen.	Oxygen.	Volume of oxygen present in amount required.
1 vol. ..	2·30	1	nil	nil
1 ,, ..	2·30	5	1	0·38
1 ,, ..	2·27	4	1	0·45
1 ,, ..	2·02	3	1	0·50
1 ,, ..	1·49	2	1	0·50
1 ,, ..	1·00	1	1	0·50
1 ,, ..	0·50	nil	1	0·50

It is evident that until the percentage of oxygen reaches the amount present in the atmosphere, the diluting influence of the nitrogen is so strong that it prevents the oxygen having any practical effect in destroying luminosity; but that as soon as the quantity of oxygen present has risen above 25 per cent, then its activity has so far overcome the diluting influence of the nitrogen that the latter has ceased to exercise any retarding influence on it.

In the case of other gases the results are as follows:—

1 vol. of coal-gas requires 0·5 vol. of oxygen.
" " 1·26 " carbon dioxide.
" " 2·30 " nitrogen.
" " 2·27 " air.
" " 5·11 " carbon monoxide.
" " 12·4 " hydrogen.

It is shown by experiment that dilution has the effect of destroying luminosity by greatly increasing the temperature necessary to decompose heavy hydrocarbons with liberation of carbon, so that at the temperature existing in a flame a volume of gas which undiluted will deposit 0·22 grm. of carbon, when diluted with 2·3 vols. of nitrogen will only deposit 0·0013, but the higher the temperature the less is the retarding action.

Experiments are next described in which the effect of the surrounding air on a flame is examined, and it is shown that, although the air introduced into a Bunsen is capable of bringing about certain changes in the flame when already burning in air, yet that it is quite unable by itself to keep the flame burning.

When a Bunsen burns under normal conditions, it has a bluish central zone, but if the air supply be largely in excess of that required for non-luminous combustion, the flame becomes smaller and fiercer with formation of a green central zone, which marks the change from a combustion in which the diluting influence of the nitrogen is still playing a certain part in causing non-luminosity, to a combustion in which the oxygen present having exceeded 0·5 vol. for each volume of gas, the nitrogen has ceased to exert any retarding influence.

By means of a platinum, platinum-rhodium thermocouple, the temperature was determined in various parts of a non-luminous Bunsen flame, burning 6 cubic feet of coal-gas per hour.

Point in flame.	Flame rendered non-luminous by—			Luminous flame. from Bunsen.
	Air.	Nitrogen.	Carbon dioxide.	
¼ inch above burner	54°	30°	35°	135°
1¼ " "	175	111	70	421
Tip of inner cone ..	1090	444	393	913
Centre of outer cone	1533	999	770	1328
Tip of outer cone ..	1175	1151	951	728
Side of outer cone level with tip of inner cone	1333	1236	970	1236

A determination was made of the temperatures existing during the normal and also the "green centre" combustion of a Bunsen:—

	Blue inner cone.	Greenish inner cone.
Tip of inner cone	1090° C.	1575° C.
Centre of outer cone	1533 "	1600 "
Tip of outer cone	1175 "	1545 "
Side of outer cone level with the tip of inner cone	1333 "	1511 "

Analyses of gases extracted from luminous flames at the points at which the temperatures had been determined show that in the inner zone there is a rapid diminution in the quantity of hydrogen as the gases ascend in the centre of the flame, a slow diminution in the quantity of the unsaturated and saturated hydrocarbons, and a large increase in the quantity of carbon monoxide in the first half of the flame. Analysis also revealed the fact that the outer non-luminous zone of a flame is not an area of complete combustion, but a portion of the flame in which the rapid entrance of air cools, dilutes, and finally puts out the flame, allowing not inconsiderable amounts of methane, carbon monoxide, acetylene, and even hydrogen, to escape unburnt.

The undoubted presence of acetylene in the products escaping from the flame, and the fact that the incomplete combustion of hydrocarbon gases always gives rise to the formation of this compound, suggested the idea that it might play an important part in the changes taking place in the interior of a flame, and experiments were made to ascertain if any appreciable quantity were formed during the destruction of the hydrocarbons in the flame gases.

	Total unsaturated hydrocarbons. Per cent.	Containing acetylene. Per cent.
Gas in burner	4·38	0·035
¼ an inch above rim of burner .	4·00	0·340
1½ inches " " .	1·53	0·560
Tip of inner cone	1·98	1·410
Centre of luminous zone	0·45	0·045
Tip of luminous zone	nil	nil

It would therefore seem that in the interior of the luminous flame the hydrocarbons are at once attacked by the small proportion of air which penetrates into the inner zone and that their incomplete combustion gives rise to acetylene, which by the time the top of the inner non-luminous cone is reached, constitutes over 70 per cent of the unsaturated hydrocarbons present, some of the acetylene, however, having probably been formed by the interaction of methane and carbon monoxide. A small proportion of some more stable unsaturated hydrocarbon may remain undecomposed and penetrate into the luminous zone, but the chief effect is due to the acetylene which is decomposed by the higher temperature, and the liberated carbon being for a moment heated to incandescence gives luminosity to the flame.

In the case of a flat luminous flame from a No. 7 Bray burner, the following results were obtained:—

Portion of flame.	Total unsaturated hydrocarbons. Per cent.	Containing acetylene. Per cent.	Other unsaturated hydrocarbons. Per cent.
¼ an inch from burner	3·565	0·115	3·450
1½ inches "	2·063	1·303	0·760
1¾ " "	1·393	1·133	0·260
2¼ " "	trace	trace	nil

The author, therefore, regards the formation and decomposition of acetylene as the main cause of luminosity in a hydrocarbon flame, and if it be necessary for purposes of simple description to divide the luminous flame into zones, he thinks it would be most accurately regarded as consisting of three, viz:—

I. The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to about 1000° C. at the apex of the zone; in this portion of the flame various decompositions and interactions occur, which culminate in the conversion of the heavier hydrocarbons into acetylene, carbon monoxide being also produced.

II. The luminous zone, in which the temperature ranges from 1000° C. up to a little over 1300° C. Here the acetylene formed in the inner zone becomes decomposed by heat with liberation of carbon, which at the moment of formation is heated to incandescence by the combustion of the carbon monoxide and hydrogen, thus giving luminosity to the flame.

III. The extreme outer zone. Here, combustion being practically completed, the cooling and diluting influence of the entering air renders a thin layer of the flame non-luminous, finally extinguishing it.

This description of a luminous flame is of necessity far from complete, as it leaves out of consideration the causes which lead to the formation of the acetylene and the numerous interactions which take place between the products of combustion and the carbon in the upper zone of the flame.

The various actions which tend to cause the loss of luminosity in a Bunsen burner, in the author's opinion, may be summarised as follows:—

I. The chemical activity of the atmospheric oxygen, which causes loss of luminosity by burning up the hydrocarbons before they, in their diluted condition, can afford acetylene.

II. The diluting action of the atmospheric nitrogen, which, by increasing the temperature necessary to bring about the partial decomposition of the hydrocarbons, prevents formation of acetylene, and in this way will, by itself, cause non-luminosity; in the normal Bunsen flame it acts by doing this until destruction of the hydrocarbons by oxidation has taken place.

III. The cooling influence of the air introduced, which is able to add to the general result, although the cooling is less than the increase in temperature brought about by the oxidation due to the oxygen in the air.

IV. In a normal Bunsen flame the nitrogen and the oxygen are of about equal importance in bringing about non-luminosity, but if the quantity of air be increased, then oxidation becomes the principal factor and the nitrogen practically ceases to exert any influence.

Discussion.

Professor Smithells said he thought Professor Lewes had made an important contribution to the subject of flame, though, perhaps, some of his conclusions were rash and open to criticism. He directed Professor Lewes' attention to the controversy on the cause of delumination of flames which had taken place between Blochmann and Heumann (*Annalen*, ccvii., 167; *Ber.*, xiv., 1250, 1925, 2210), in which the whole question was very fully discussed and dealt with in a quantitative manner; also to Waldie's observations (*Phil. Mag.* (1838), No. 13, p. 88), in which delumination was effected by introducing luminous flames into atmospheres containing gases neutral to combustion. Waldie also made quantitative measurements, and sought to establish a relationship between diffusibility and deluminating effect. The abnormally great effect of carbon dioxide in destroying luminosity had been generally attributed, not to its high specific heat, but to its power of taking up carbon. Thus, for example, when mixed with an equal volume of ethylene in a flame, it was supposed that it underwent conversion into an equal volume of methane and a double volume of carbon monoxide—both of which would burn with practically non-luminous flames. Professor Lewes was in error in stating that Davy limited his theory to flames produced by hydrocarbons, for he explicitly stated that the luminosity of all flames ordinarily called luminous was to be attributed to solid particles, and in this respect left his theory open to Frankland's correction; he was also wrong in supposing that the theory that carbon is separated in a flame, owing to preferential combustion, was no longer held: it was, on the contrary (as the speaker could vouch from careful investigation), very widely accepted and taught. In a paper which is in the press it would be clearly demonstrated, he thought, that there are four distinct regions in a flame, however many gradations of chemical change there may be. He considered that the most important point in the paper which they had heard was that relating to the presence of acetylene in the flame. In his own experiments with ethylene he had also found that during luminous combustion scarcely any other hydrocarbons than acetylene are present in the aspirated gases. He was not satisfied, however, with Professor Lewes' proof of the escape of acetylene from ordinary luminous flames; whilst there was no *a priori* evidence against such an occurrence, unless the extraction of acetylene had been effected otherwise than by introducing cold aspirating tubes into the flame, it might be that the production of acetylene was a consequence of the method of experiment—it being well known that acetylene escaped freely from flames in contact with metallic surfaces. Accepting it as proved that the formation of acetylene in flames was an important factor in the origin of luminosity, the question was by no means worked out. It remained to discover exactly what became of the acetylene. Professor Lewes had kindly left the solution of this problem to the speaker, who, however, on his part, expressed a desire not to lay claim to too much undiscovered country, or to preclude Professor Lewes from the natural continuation of his interesting investigation.

Professor Lewes, in reply, said that he was perfectly aware of the work done by Heumann, Blochmann, Stein, and Wibel. He must, however, dissent from the assumption that they had given quantitative proofs of many of their assertions.

The theory that carbon dioxide acted in destroying luminosity by converting ethylene into carbon monoxide and methane was, he thought, disproved, both by the experiments on the effect of heat in restoring luminosity to the flame and by the thermal changes taking place, as shown by the temperature of the diluted flame.

Undoubtedly Sir Humphry Davy went rather too far in his theory of luminous flames; but in a paper on the subject by him, in the *Phil. Mag.* for 1817, he says: "The intensity of light of flames depends *principally* upon the production and ignition of solid matter in combustion," also "Flame is gaseous matter heated so highly as to be luminous," and "when in flames pure gaseous matter is burnt, the light is extremely feeble," so that it seems hardly just to insist that he considered solid matter *absolutely essential* to luminosity.

The determination of the combustible gases escaping unburnt from the outer zone of non-luminous flames had been made by taking a platinum tube 2 m.m. in diameter, bent into a ring, and pierced on the inside with minute holes; this ring was placed round the flame, but not in contact with it, and the products of combustion were aspirated through this, so that the acetylene could not be due to the action of the tube.

The speaker regarded the conversion of the hydrocarbons into acetylene as the chief cause of luminosity in flame, because acetylene was practically the only heavy hydrocarbon present in that part of the flame where luminosity commenced, and as it was known that acetylene was an endothermic compound, which could be decomposed by detonation, it seemed highly probable that it would be readily decomposed by heat and liberate carbon.

With reference to Mr. Groves's remark that when a Bunsen burner is alight at the bottom, a non-luminous flame is produced, as the acetylene escapes unburnt, such a flame could only have a low light value.

*95. "*The Origin of Flame Colouration. A Preliminary Notice.*" By A. Smithells.

The author has found that the two cones of non-luminous flames separated widely from one another by the apparatus recently described by him in conjunction with Mr. Harry Ingle (*cf. Proc. Chem. Soc.*, 1891, p. 159), are differently affected by certain flame-colouring compounds. The most conspicuous case is that afforded by copper salts. In the inner cone of such a flame, copper salts produce no effect or only a lurid luminosity, without the slightest tinge of green, whilst in the outer flame the usual green colour is fully developed. Similar differences are noticed when using manganese salts. On introduction of gold chloride, the outer flame assumes a green and a blue tinge; the green, which is said to be the colour characteristic of gold salts, is not observable in the inner flame, but only a blue colour and general luminosity. The

salts of the alkalies and alkaline earths appear to affect both cones alike.

As the inner cone is very much hotter than the outer one, the non-development in the former of the usual colouration is not to be attributed to any deficiency in temperature. The only explanation which suggests itself is that in some cases at any rate the colouration of flames is not to be attributed to the mere volatilisation of salts and the incandescence of their dissociated or undissociated vapour, but to a *flash* accompanying chemical combination. The particular combination, which in the case of copper gives rise to a green flame, may be that of the metal with oxygen. In the experiment cited, the inner cone of flame is surrounded by an atmosphere of carbon monoxide and dioxide, hydrogen, and water, which is capable of reducing copper compounds, even at a red heat, whereas the outer cone is surrounded by oxygen. The view here advocated is confirmed by the effects noticed on introducing copper oxide dust into the gas-supply. As the dust passes through the inner cone, a mere general luminosity due to solid particles is noticed, but when it reaches the outer cone it colours this a bright green. The copper oxide appears therefore to be reduced to metal in the inner cone, and to be re-oxidised in the outer one, the act of oxidation giving rise to the green flash of light.

The hypothesis here broached, that flame colourations are due in some cases to chemical actions, and are not mere physical effects, requires for its support a greater array of facts and much more careful investigation than are here recorded. The author is engaged in extending the investigation, and only brings the matter forward at the present time after hearing that the flame-separating apparatus is likely soon to come into general laboratory use.

*96. "*Note on the Action of Dilute Nitric Acid on Coal.*" By R. J. Friswell.

In the last number of the *Berichte* (1891, p. 4085), Luzi has described the action of nitric acid on graphite, certain varieties of which, on treatment with the strongest fuming acid, yield a product which "puffs" like a nitro-compound when heated on platinum foil, and then swells out into prolonged vermiform coke-like masses. The writer feels that the substance in question sufficiently resembles one he has quite lately discovered to cause him to communicate the following note:—

If bituminous coal in fine powder be covered with rather more than double its weight of 49 per cent nitric acid, the mass rapidly becomes warm, and dense red fumes are given off. If 90 grms. of coal and 200 c.c. of the acid are taken, the action is extremely brisk and the frothing so violent that a 2000 c.c. flask is requisite to contain the mass. In about thirty minutes the action slackens, and heat being now applied the action is kept going at such a rate that a brisk evolution of gas continues; the solution is gradually raised to the boiling-point and there maintained, the total time occupied being about six hours. The whole is now diluted, poured into a filter, and well washed. The filtrate consists of dilute nitric acid, with salts of calcium, iron, &c., in solution. The black residue on the filter is apparently unchanged coal. When washed free from acid, the residue is introduced into a flask and boiled with a dilute solution of sodium carbonate; nearly the whole dissolves, carbonic anhydride being briskly evolved. The resulting deep black-brown coloured liquid filters with great difficulty, but by careful treatment with water in deep vessels the insoluble matter from the 90 grms. of coal was found to be 12·5 grms., consisting of coarse particles of coal, sand, &c.

One grm. of coal, ground in an agate mortar and similarly treated, left only a trace of insoluble matter, so that, in some varieties of coal at least, the whole of the organic matter of the coal undergoes change.

The filtered solution on acidification with (preferably) hydrochloric acid, deposits a bulky, deep brown-black, flocculent precipitate, which is difficult to wash; it is insoluble as long as the wash-water contains small quantities of metallic salts or acids, but dissolves somewhat freely as the washing proceeds. In boiling distilled water it is fairly soluble, and separates therefrom on cooling in deep brown flocks.

The washed acid dried at 100° forms brilliant, black, friable masses, showing bright conchoidal fractures. If heated on platinum foil it puffs, swells slightly, and leaves a residue of carbon rather more bulky than its original mass, and almost as brilliantly black. The puffing is very like that of a nitro-compound with a very high carbon ratio; attempts to reduce it with zinc dust and caustic soda and with sodium amalgam have hitherto failed, and so have similar attempts with acid reducing mixtures. The presence of nitrogen is indicated in the usual manner on heating it with sodium; on submitting it to dry distillation with zinc dust, hydrogen and cyanogen are evolved, a small aqueous distillate, smelling of ammonia and faintly of pyridine, and containing a very large quantity of hydrocyanic acid, being also obtained.

If the black acid be further treated with nitric acid, a brown acid is formed, which has not yet been examined.

At first sight the product appears to bear considerable analogy to the humic and ulmic acids described in vol. xv. of "Gmelin's Handbook," particularly the one known as Sprengel's humic acid, obtained by extracting peat with ammonia. It, however, differs very much from that product in several particulars. It is not hygroscopic, it does not become insoluble on drying, and it does not yield acetic acid on dry distillation. As to the other humic acids, the substance from coal does not yield ammonia when boiled with alkalies, as they all, or nearly all, are said to do.

Lastly, there is very strong evidence in favour of the new product being a nitro-compound.

The possibility of attaining some evidence through the study of the substance in question as to the character of the constituent of coal from which it is derived is obvious.

97. "*A Pure Fermentation of Mannitol and Dulcitol.*" By Percy F. Frankland, F.R.S., and Wm. Frew.

The authors have obtained a micro-organism which sets up a fermentative decomposition not only of mannitol but also of dulcitol, which has not hitherto been subjected to pure fermentation, and which has been found to resist the fermenting bacteria with which they have hitherto experimented.

The products of the activity of this organism are essentially the same in the case of the two substances in question, consisting of ethyl alcohol, acetic acid, succinic acid, carbonic anhydride, and hydrogen, a notable proportion of formic acid being also obtained when the fermentation occurs in the absence of air and under slight pressure.

The carbonic anhydride and hydrogen evolved are approximately in the proportion of equal molecules or in that in which they are present in formic acid, and owing to the variable quantities in which the formic acid was discovered in the several fermentations, it is believed that more or less of the formic acid at first produced is subsequently decomposed with evolution of equal numbers of molecules of carbonic anhydride and hydrogen. This is the more probable, as in each of the fermentations the sum of the formic acid, hydrogen, and carbonic anhydride approximately corresponds in molecules of formic acid to the amount of alcohol in molecules produced in the same fermentation.

The decomposition of the dulcitol and mannitol may be regarded as involving two independent sets of changes, viz., (*a*) $C_6H_{14}O_6 = 2C_2H_6O + CO_2 + CH_2O_2$ and (*b*) $C_6H_{14}O_6 = C_4H_6O_4 + C_2H_4O_2 + 2H_2$; but from the proportion which the acetic acid bears to the alcohol, it appears that two molecules are resolved in accordance with equation (*a*) for every one that is decomposed according to (*b*). The only marked discrepancy is in the case of the succinic acid, which was only found to about half

the extent demanded by the equations given, but this discrepancy is probably due to the difficulty attending the accurate determination of succinic acid in a complex mixture of substances such as was present in these experiments.

In view of the products to which this organism gives rise, the authors propose for it the name of *Bacillus ethacetosuccinicus*. A detailed account of its morphological characters by Mrs. Percy Frankland is appended to the paper.

The authors mention that incidentally a compound was discovered of dulcitol with calcium chloride,—

$$C_6H_{14}O_6,CaCl_2.$$

98. "*Synthesis of Hexahydroterephthalic Acid.*" By J. E. Mackenzie and W. H. Perkin, Jun., F.R.S.

By eliminating two molecules of carbon dioxide from the hexamethylenetetracarboxylic acid obtained in the form of ethylic salt by the interaction of ethylene bromide and the disodium derivative of ethylic butanetetracarboxylate, the authors have obtained as chief product the sparingly soluble hexahydroterephthalic acid of von Baeyer, together with a small amount of what is probably the isomeric acid.

99. "*The Magnetic Rotation of Dissolved Salts.*" By W. Ostwald.

In a former paper (*C. S. Trans.*, 1891, p. 198) I pointed out that the unexpected results which Dr. Perkin obtained in his investigations on the rotatory power of solutions might be explained by means of Arrhenius's electrolytic dissociation theory, at the same time suggesting that the rotatory power of the ammonium salts of weak acids would probably show marked deviations from the calculated values.

Dr. Perkin, however, states in a recent communication (*ibid.*, 1891, p. 981) that such deviations do not exist, the actual differences being very small and comparable with those attending the formation of the ethereal salts of the same acids. Although I must confess that this result is contrary to my expectations, I am anxious to point out that the fault is mine, and not that of the dissociation theory. According to this theory, the condition of a substance is very different according as it can act as an electrolyte or not, *e.g.*, sodium chloride in the solid state or in aqueous solution; hydrogen chloride dissolved in amylic oxide (where it is a non-electrolyte) or in water, &c. In the case of the magnetic rotations of haloid salts, the differences foreshadowed by the dissociation theory are apparent as very considerable differences from the calculated values, and inasmuch as the former views did not take any account of such differences, I was right in saying that the dissociation theory is alone in accordance with Dr. Perkin's observations. The values for oxy-acids also differ from the calculated values, though in a much less degree; I expected such differences to be manifest also in the case of ammonia and the fatty acids, but Dr. Perkin has shown that the differences are quite insignificant.

As the dissociation theory does not lead to any numerical value or sign of the differences, the very low values observed by Dr. Perkin in the case of the fatty acids are not contrary to the theory, but suggest only the interesting question: on what qualities does the sign and the value of the variation of magnetic rotation attending the transition of non-electrolytic molecules into ions depend? In the case of haloid acids and salts, the variation is positive; in the case of the oxy-acids, negative; therefore, it is not surprising that molecules with nearly zero variations are also capable of existence. Investigation of a greater number of such cases will certainly throw light on this question.

A tolerably short method of testing whether my attempt to explain the facts of magnetic rotation by the dissociation theory is tenable, is the following:—As the greatest differences are observed in the case of halogens between the ionic and the non-ionic state, an investigation of electrolytes containing halogen atoms, but not as ions, appears to promise most, *e.g.*, the salts of mono-, di-, and trichloracetic acids, of chloric and iodic acids, potassium mercuric iodide, K_2HgI_4, &c. If in all these cases abnormal high values for the halogens should be obtained, I should not hesitate to confess that I have been on a false track.

100. "*The Dissociation of Nitrogen Peroxide.*" By W. Ostwald.

Availing himself of the data recently given by Cundall (*C. S. Trans.*, 1891, 1076), the author has compared the extent to which this compound undergoes dissociation when vaporised with that which it suffers when dissolved in chloroform; from the results he concludes that it behaves in accordance with Van 't Hoff's generalisation that dissolved substances obey the same laws as gases. It appears, however, that in the gaseous state dissociation is far more advanced than in a chloroform solution.

101. "*Corydaline.*" (I.) By James J. Dobbie, M.A., D.Sc., and Alexander Lauder.

Analyses of the alkaloid, as well as of its salts and derivatives, led Herm. Wicke (*Annalen*, 1866, cxxxvii., 274) to assign to corydaline the formula $C_{18}H_{19}NO_4$. The authors have purified samples by repeated re-crystallisation from a mixture of alcohol and ether, and have obtained the alkaloid in the form of flat, prismatic, colourless crystals, melting at 134·5°. In analysing it, they obtained results irreconcilable with Wick's formula,—

$$C_{18}H_{19}NO_4,$$

and propose instead the formula $C_{22}H_{28}NO_4$.

The iodhydride is easily obtained in pale yellow coloured prisms by re-crystallising from water the precipitate obtained when a solution of potassium iodide is added to one of corydaline hydrochloride.

The platinichloride and corydaline methiodide were prepared by the methods described by Wicke.

The results obtained on analysing these compounds corroborate those afforded by the alkaloid.

When heated with hydrogen iodide, one formula-weight of corydaline yields four molecular proportions of methyl-iodide, together with the iodhydride of a base which apparently bears the same relation to corydaline that papareroline bears to paparerine. On oxidation with potassium permanganate, corydaline yields a number of products which the authors are now engaged in investigating.

102. "*Silver Compounds of Thiourea.*" By J. Emerson Reynolds, F.R.S.

In a paper on some derivatives of thiourea, published by the author in 1888 (*Trans.*, liii., 857) it was pointed out that a crystalline compound of silver bromide with thiourea, viz., $(CSN_2H_4)_2AgBr$, was obtained by the interaction of equimolecular proportions of silver nitrate and the new compound then described, $(CSN_2H_5)_4NBr$. It was further stated that analogous compounds with other silver salts had been obtained by the same method as well as by direct union with thiourea, and that their detailed examination had cleared up certain obscure facts which were simply recorded in the author's earlier papers on thiourea.

The publication of a paper on the subject was deferred in the expectation of the completion of a new examination of the more interesting gold and platinum compounds, but the appearance of a paper by Kurnachow in a recent number of the *Berichte* on silver compounds of thiourea renders further delay undesirable, as that chemist refers only to the author's paper on thiourea, published 22 years ago.

In the course of the work of 1888, referred to above, the writer obtained the following compounds:—

$(CSN_2H_4)_2AgNO_3$. Beautiful long needles, melting at 141°, decomposing at 150° with separation of Ag_2S. Best obtained from an alcoholic solution containing 4 mols. thiourea to 1 mol. silver nitrate.

$(CSN_2H_4)_2AgNO_3$, a product of the partial decomposition of the previous compound by water.

$(CSN_2H_4)AgNO_3$, a precipitate obtained on mixing equimolecular proportions of its constituents. This is decomposed by water; and the author regards the silver precipitate mentioned in his 1869 paper as the probably indefinite product of too carefully washed 1 : 1 compound above mentioned: this being the view also taken by Kurnachow.

$(CSN_2H_4)_2AgBr$, fine prisms melting at 120—121°.

$(CSN_2H_4)AgBr$, a white powder.

$(CSN_2H_4)_2AgCl$, crystalline; melts at 170—171°, decomposing at 180°. This was also obtained by Volhard.

No 1 : 1 compound was obtained with AgCl.

$(CSN_2H_4)AgI$, a white crystalline precipitate. In this case the higher compound appears only to exist in solution of thiourea.

$(CSN_2H_4)_2AgCN$. Small crystals which discolour at 115° and melt to a dark liquid at 126° sharply.

All the foregoing substances readily afford Ag_2S when heated a few degrees beyond their melting points, or even before melting, as in the case of the silver cyanide compound.

Anniversary Meeting and Second Anniversary Dinner.

The Anniversary Meeting will be held at *Four o'clock in the Afternoon* of Wednesday, March 30th next.

It is arranged that on the evening of the same day the Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Métropole.

NOTICES OF BOOKS.

The Phosphates of America: Where and How they Occur, How they are Mined, and What they Cost. With Practical Treatises on the Manufacture of Sulphuric Acid, Acid Phosphate, Phosphoric Acid, and Concentrated Superphosphates, and Selected Methods of Chemical Analysis. By Francis Wyatt, Ph.D. Second Edition. New York: The Scientific Publishing Co.

This is a very comprehensive work. After general remarks on phosphates and their assimilability, the author proceeds to his more special subject, the phosphates of North America. Here we must refer to a practical defect for which the publishers only can be held responsible. The running title at the head of each page is the same throughout, "The Phosphates of America." It would, we submit, have been a great convenience for the reader if these words had been placed at the top of the left hand page only, giving on the right hand the special subject of the chapter. This would be the more useful as there is no table of contents. Chapter III. is taken up with an account of the apatite deposits of Canada and their present exploitation. Chapter IV. describes the phosphate beds of South Carolina. We are told that "the known available and readily accessible deposits are all appropriated," and that the mines will, at the present rate of production, be all exhausted in about twenty-eight years from the present time. In Chapter V. follows a description of the deposits of Florida; whilst these deposits are of immense extent, and while they yield a material well suited for the manufacturer, a word of warning is thrown out which we cannot discuss, but which will be very salutary to intending investors.

Chapter VI. describes the manufacture of sulphuric acid, including the construction and use of the Glover tower. We regret to find that the writer persists in the use of the Beaumé hydrometer,—an instrument which has no advantages to compensate for its unquestionable defects.

In Chapter VII. we come to the manufacture of superphosphate, phosphoric acid, and high grade supers. Dr. Wyatt pronounces the rejection of mineral phosphates containing more than a certain limit of iron and alumina, *i.e.*, 3 per cent, a "foolish prejudice." As a "dryer" he adds to the material "finely-powdered chalk or any other cheap and available source of carbonate." It is undeniable that an escape of CO_2 lightens the texture of the superphosphate. The custom of calcining Florida phosphate he considers "unscientific and harmful," since the presence of free lime retards the drying action. Some makers, however, after calcining, treat with an excess of water, thus dissolving away the lime and enriching the raw material.

The plant for the manufacture of superphosphate is described, and well figured. The author strongly recommends high grade superphosphates made with phosphoric instead of sulphuric acid, the economy of which he demonstrates at length. The only difficulty lies in getting the consumer to recognise its merit, and to pay a fair price for it.

The fumes given off from superphosphate works have not escaped public notice in the United States, and Dr. Wyatt accordingly gives a drawing of an absorption apparatus.

As regards the analysis of materials, the author gives processes for determining moisture, combined water and organic matter, silica, phosphoric anhydride, SO_3, fluorine, lime, magnesia, carbonic anhydride, iron, and alumina. For the determination of carbonic anhydride he prefers the apparatus and method of Scheiller. The volumetric processes for determining phosphoric acid he has discarded for commercial purposes, though he retains the uranium method as a factory guide.

In his method of analysing pyrites we may mention as something exceptional that he determines the copper he precipitates as the white sub-sulphocyanide.

In the table of atomic weights, stated as being according to the latest determinations, platinum is still given as higher than gold. The work may be pronounced a very useful manual of reference.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—As your columns have always been open to any discussion which tends to the advancement of our profession may I ask for space to draw attention to a "circular" signed by Mr. William Thomson, of Manchester, and recently sent to Members of the Institute, inviting them to turn out the Council and elect one nominated by Mr. Thomson and his committee. My object in doing this is to point out two of the many inaccuracies in the letter.

No. 1.—The circular quotes, or rather misquotes, p. 7 of the Charter as follows:—

> "The elevation of the profession of Analytical Chemistry and the promotion of the efficiency and usefulness of persons practising the same."

In the original it reads "profession of *Consulting* and Analytical Chemistry."

As the omission of this word—and indeed the whole tenour of the circular—would make it appear as if the Institute were founded for the advancement of Analysts rather than of the Chemical profession, ill-natured people might be inclined to think that this strange perversion of the wording of the Charter was not entirely undesigned on the part of the authors of the circular.

No. 2.—Under the heading "*Fourth*," the circular reads—"A distinct pledge was given that the papers and discussions of last year's conferences should be published."

This statement is—to speak quite plainly—untrue. The only document I can find relating to the matter is the notice issued by the Institute and dated December 11th,

1891, for the purpose of calling a meeting to consider the ethics of professional certificates. And this says—"The Council hope you will be able to attend" . . . "as a full report of the proceedings will *not* be published" (the italics are mine). This "*not*," like the word "Consulting" previously alluded to, seems to be ignored by the gentlemen who drew up the "circular."

The names of some fifty members of the Institute, nearly all public analysts, are appended to this circular, but I feel sure that neither Mr. W. Thomson nor these gentlemen would have consented to their names being attached to a document which they knew contained garbled quotations or untrue statements. There can be little doubt, therefore, that those who drafted the circular, and are responsible for the "inaccuracies" in it, considered "a policy of secrecy and silence" to be best when they were persuading their friends to allow their names to appear as approving of the circular.

It is to be hoped that the Members of the Institute at large will do their best to frustrate this attempt to hand over the Institute bound hand and foot to the public analysts, or rather to the small and noisy "party of progress" (?) who form but an exceedingly small fraction of the large body of professional chemists, to protect whose interests the Institute was founded.—I am, &c.,

CHARLES E. GROVES.

Guy's Hospital, London,
February 8, 1892.

THE DENSITIES OF SULPHURIC ACID.

To the Editor of the Chemical News.

SIR,—Owing to my not asking for a revise of my paper in CHEM. NEWS, vol. lxv., p. 13, a few errata have remained, as "leader" in lieu of "teacher," (p. 13) and "lowest" freezing point in lieu of "highest" (p. 14). The latter is so obviously a slip of the pen that nobody but Professor Pickering would have construed it as a "misrepresentation" as he does in his letter at p. 50. His letter, in which he does not even retract the charge of *wilful* misrepresentation, puts him more than ever out of court for any further discussion in the columns of a scientific journal. I have only to add that any reader of No. 1676 will discover more than one reason why Prof. Pickering's assertion of having attained an *actual* accuracy of 0·01 per cent in his sulphuric acid tables is utterly untenable. I for my part have done with him.—I am, &c.,

GEORGE LUNGE.

Zürich, January 27, 1892.

OBITUARY.

THE LATE DR. A. J. BERNAYS.

THE death of Dr. Bernays, which was announced in the *Times* of January 9th last, removed from our midst one whose loss is very sincerely mourned by those who had the privilege of his acquaintance. Dr. Bernays was a lucid lecturer and a capital experimentalist; and the rare combination of tact and urbanity with which his lectures were delivered gained him the respect of, and gave him a remarkable influence over, the rawest and most unruly "first year's man." Dr. Bernays began his professional career as a lecturer on chemistry and analyst in the town of Derby, and was lecturer at St. Mary's Hospital, Paddington, prior to his appointment to the chair of chemistry at St. Thomas's Hospital, which he occupied for the long period of thirty-one years. He also held some important analytical appointments, and wrote several works on chemistry, among them the very complete, yet concise, "Notes on Analytical Chemistry." Dr. Bernays had, in addition, been Examiner in Chemistry to the Colleges of Physicians and Surgeons. In private life his charming manners and old-fashioned courtesy endeared him to all who knew him; and it can be truly said that, in addition to being an excellent chemist and an amiable teacher, he was a good man in every sense of the word.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 4, January 25, 1892.

Report on the Deplastering of Wines.—The commission named to examine the question (MM. Berthelot, Gautier, and Duclaux), proposes to reply to the inquiry of the Syndical Chamber of the Wine and Spirit Trade, that the Academy cannot give its approval to the use of strontium salts for deplastering wines, and that it condemns this practice.

The Determination of Molybdenum.—E. Péchard.—This paper will be inserted in full.

The Stereochemistry of Diacetyl Tartaric Acid.—Albert Colson.—The author holds that the notation based on the properties of the regular tetrahedron is insufficient for the representation of the active bodies, and may lead to incorrect previsions.

On Certain Soluble Colouring-Matters Produced by Bacteria in Medical Distilled Waters.—L. Viron.—This paper will also be inserted in full.

On the Occurrence of Phenomena of Nitrification in Media Rich in Organic Matter and having an Acid Reaction.—E. Chuard.—The existence of relatively active nitrification in peat-mould (turf mull) is not without agricultural importance. It is merely necessary to dig up some time beforehand the peat earth, to break it up, and store it in heaps as permeable as possible, but secure from rain in order to have a manure rich in active ammonia.

Ammonia in Rain-Water and in the Atmosphere.—A. Muntz.—In opposition to Albert Lévy the author adheres to his results and those of M. Marcano on the richness of rain-water in ammonia in tropical countries.

MISCELLANEOUS.

The Journal of Inorganic Chemistry.—It is a matter of complaint that communications on inorganic chemistry are at present to be met with scattered through a great number of journals and transactions, where they appear almost as aliens amidst the constantly increasing host of researches on the chemistry of the carbon compounds. This circumstance greatly retards and discourages the study of the other elements, and consequently prevents the harmonious development of the science as a whole. We must remember that, especially since the establishment of the periodic system, inorganic chemistry can no longer be regarded as a merely descriptive science, just as it has been the case with zoology and botany since the promulgation of the doctrine of evolution. Hence a journal is about appearing under the editorship of Prof. Gerhard Krüss, of Munich. Here will be brought forward besides inorganic researches theoretical memoirs in so far as they touch the field of inorganic chemistry, analytical investigations, brief abstracts of papers on inorganic, analytical, and physical chemistry, so that every advance made in the entire scope of inorganic chemistry may here be traced by the reader. The journal will include among its co-operators Berthelot, Blomstrand,

Brauner, Clarke, Classen, Cleve, Cooke, Cossa, Crookes, Ditte, Friedheim, Gibbs, Hempel, Joergensen, Kraut, Lunge, Mallet, Mauro, Mendeleeff, Meyer, Mond, Nilson, Piccini, Roscoe, Seubert, Spring, Thorpe, Winkler, and other colleagues. The journal will be published by Leopold Voss, Hamburg, Hohe Bleichen, 18.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Platinum.—Will any reader conversant with the facts kindly answer the following?—(1) The reason of the recent high price of platinum; (2) The reason of the sudden fall in price; (3) Is there any ground for supposing such a violent fluctuation will occur again within any reasonable time?—M. A. S.

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Medical, 8.30.
— Society of Arts, 8. "Developments of Electrical Distribution," by Prof. George Forbes, F.R.S.
TUESDAY, 16th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "The Forthcoming Exhibition at Kimberley, South Africa," by Mr. Lewis Atkinson.
WEDNESDAY, 17th.—Society of Arts, 8. "The Pamirs," by Capt. F. E. Younghusband.
— Meteorological, 7.
— Microscopical, 8.
THURSDAY, 18th.—Royal, 4.30.
Royal Society Club, 6.30.
— Royal Institution, 3. "Some Recent Biological Discoveries," by Prof. E. Ray Lankester, M.A.
— Institute of Electrical Engineers, 8.
— Chemical, 8. Ballot for the Election of Fellows. "A Search for a Cellulose Dissolving (Cytohydrolytic) Enzyme in the Digestive Tract of Certain Grain-feeding Animals," by Horace T. Brown, F.R.S. "Limetbin," by Prof. Tilden, F.R.S.
FRIDAY, 19th.—Royal Institution, 9. "On Micro-organisms in their Relation to Chemical Change," by Professor Percy F. Frankland, F.R.S.
— Geological, 3. (Anniversary).
— Quekett Club, 8. (Anniversary).
SATURDAY, 20th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

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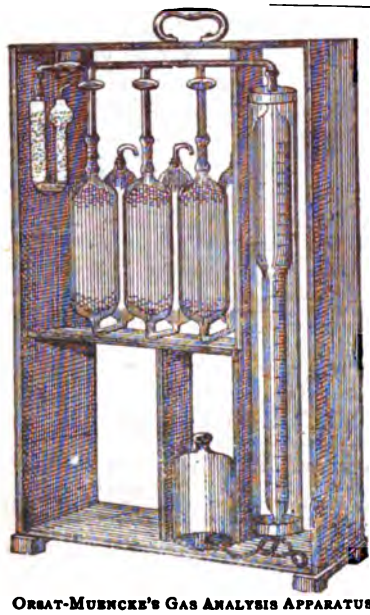

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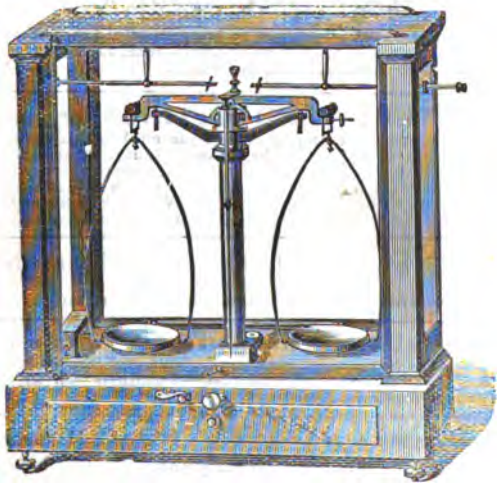

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1682.

NOTE ON THE

CONDUCTIVITY OF PEROXIDE OF LEAD.

By JOHN SHIELDS, Ph.D., B.Sc.

When a solution of sodium lead tartrate is electrolysed, hydrated peroxide of lead separates out on the positive electrode. The formula ascribed to this peroxide by Wernicke and Streintz is H_2PbO_3, and a sample which I analysed contained:—

	Found.	Theory.
PbO_2	93·46	93·0
H_2O	6·54	7·0
	100·00	100·00

which corresponds sufficiently well with the theory.

In order to decide whether peroxide of lead and its hydrate conduct electricity like the metals or like electrolytes, pure peroxide was prepared by Wöhler's method (*Journ. fur Prakt. Chemie*, vol. xc., p. 383), whilst the hydrate was deposited electrolytically from a solution of sodium lead tartrate on a sheet of platinum. The hydrate was washed thoroughly with water, alcohol, and ether, and allowed to lie in the air until its weight remained constant, when it possessed the composition given above.

The first method employed was the following. The chemically and electrolytically prepared peroxides were pressed into circular discs 13·3 m.m. in diameter, which were then firmly clamped between two platinum plates connected with a battery. After the current had passed for a considerable time the battery circuit was broken and at the same moment the plates were placed in connection with a sensitive galvanometer. Although the experiments were repeated several times, no deflection of the galvanometer could be observed. Now, if either of the peroxides conducted electrolytically, decomposition would have ensued on passing the current of electricity, and consequently a polarisation current would have been obtained on breaking the battery circuit and connecting with the galvanometer. As neither of the peroxides gave such a current we must conclude that both conduct electricity metallically.

The result stands in direct opposition to that of Streintz (*Wied. Ann.*, xli., 104), who found that chemically prepared peroxide of lead conducted like a metal, whilst the hydrated peroxide behaved like an electrolyte. I therefore determined to repeat the experiments using another method, namely, that employed by Streintz. Fig. 1 is a diagram of the arrangement. A glass tube, A, is closed at one end with a piece of clean metallic lead or platinum as the case may be, and into the tube is pressed the substance to be examined. This is connected with dilute sulphuric acid contained in the beaker, B, by means of a moist cotton thread. In the beaker stands a rod of amalgamated zinc. The difference of potential between the zinc and the lead or platinum is measured with the electrometer, E (in this case Ostwald's form of the capillary electrometer was used, and the potential difference obtained by compensation).

Now, if the substance contained in A conducts like a metal, we may replace the lead by platinum or any other metal, and the potential difference will always remain the same. On the other hand, if the substance in A is an electrolyte, we will obtain a certain difference of potential between zinc and lead, and if we substitute platinum for lead we will obtain another potential difference, and so on for all the different metals.

I found it convenient to prepare several tubes, half of which were closed at one end with freshly-scraped lead, and the other half with platinum. The following results were obtained:—

Chemically prepared Peroxide of Lead.

Potential difference	Zn—Pb	2·13 Volt.
,, ,,	Zn—Pt	2·14 ,,

Electrolytically prepared Peroxide of Lead (Hydrate).

I.

Potential difference	Zn—Pb	2·01 Volt.
,, ,,	Zn—Pt	2·02 ,,

This sample was thoroughly washed with distilled water and dried in the air.

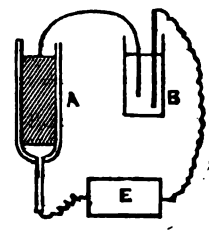
These experiments confirm the result obtained by the first method, and as this does not agree with the observations of Streintz, a fresh quantity of peroxide was prepared electrolytically; it was washed with water, alcohol, and ether, and then *at once* pressed into the tubes and the measurements made.

Electrolytically prepared Peroxide of Lead (Hydrate).

II.

Potential difference	Zn—Pb	1·92 Volt.
,, ,,	Zn—Pt	1·94 ,,

The potential differences observed are in all cases independent of the metal in direct contact with the substance examined, and therefore we must conclude that *peroxide of lead, PbO_2, as well as its hydrate, H_2PbO_3, conduct electricity in the same way as the metals.*



Opportunity was also taken to make an approximate determination of the resistance of the peroxide of lead, and no change in this was noticed on heating to 115° C.

	C.G.S. Units.
Specific resistance of the chemically prepared peroxide	5·59 × 10^9
Specific resistance of the electrolytically prepared peroxide..	6·78 × 10^9

Leipzig, December, 1891.

AN IMPROVED FORM OF INDUCTION COIL FOR SPECTROSCOPIC WORK.

By H. N. WARREN, Research Analyst.

The original construction of induction coils known as the continuous wind, constituting what is known as the secondary coil, has been of late superseded by what is termed the segment wind, differing both as regards its insulation and also in its effects when compared with the former system. The following description of a machine of this construction will afford a brief idea of the benefits derived over other systems, when every advantage is taken in manufacturing an article of this description to avoid, if possible, the use of impure elements:—

In this case the primary core was prepared by precipitating pure oxide of iron, igniting, and reducing it in a current of hydrogen gas; afterwards, fusing and forging

the same. Of this substance, 10 lbs. of wire, about the thickness of a wax match and a foot and a half in length, was selected, a pure iron rod composed of the same substance also passing through the centre. This core was covered with several layers of paraffined silk, over which was wound 4 lbs. of very thick insulated copper wire, each layer being carefully insulated; the whole being enclosed, save the extremities, in a thick ebonite tube. Upon this was mounted the secondary, consisting of 25 lbs. of No. 22 double silk-covered wire; on the whole this may be regarded as a thick wire, but the strength afforded, both as regards the spark obtained and also the amount of current allowed, was well merited. The secondary was composed of 52 segments, each separated from each other by mica plates; the whole being coated with paraffin to about two inches in depth, being further cased in ebonite. To the contact-breaker of the machine, in order to absorb the spark, was connected 500 sheets of copper foil, each being insulated by paraffined silk and protected in the usual manner. The machine, as now constructed, required five Bunsen quarts to urge it to its full. The spark thus obtained, which was nearly fifteen inches in length, was the most intense I have ever seen. In some instances, the sudden discharge was equivalent to the report of a rifle, affording a constant stream of thick fire resembling lightning. The supply of ozone liberated was very considerable, almost immediately bleaching cotton fabrics when brought near the same in a moist condition; two dozen large vacuum tubes, two feet long and upwards, were instantaneously lighted; and deal boards, to the thickness of half an inch, were readily pierced; almost every elementary substance was speedily volatilised when brought in contact with the spark, and their spectra thus revealed by the aid of that instrument.

Everton Research Laboratory,
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ON CERTAIN SOLUBLE COLOURING MATTERS PRODUCED BY BACTERIA IN MEDICINAL DISTILLED WATERS.

By L. VIRON.

In a previous investigation on the part played by Schizomycetes in the coloured reactions which occur in distilled waters (*Journ. Pharm. Chemie*, 1891), we have shown that sometimes the colouration is due to zooglœic masses suspended in the liquid (as M. Barnouvin states), but that sometimes the colouring-matter is really in solution, since the liquid traversed a Chamberland filter without a decrease of the colouring intensity.

We have been able to isolate some of these pigments in solution; we have succeeded in characterising them chemically, and in cultivating the micro-organisms which produce these colouring principles.

Our first researches were directed to an orange-flower water having a very deep green colour; on evaporation it left 70 m.grms. per cent of fixed residue,—the residue consisting of 69 m.grms. organic matter and 1 m.grm. of mineral substances. The organic matter takes the form of greenish masses, insoluble in ether, chloroform, and benzene; completely soluble in ammoniacal water or on ammoniacal ethero-alcoholic liquid (Adams's galactimetric liquid); soluble in part only in methylic alcohol; but none of these treatments yield the pigment in a crystalline state.

Under the microscope it takes the form of greenish granulations, of rods more or less elongated, and of yellowish lamellæ. From this pigment we have been enabled to isolate three distinct colouring matters, and to characterise them by chemical reagents. One of these matters has been isolated by means of methylic alcohol; it is soluble in water, to which it communicates a slight violet tint, which rapidly turns brown in the air. It is without action on the sulphocarbotic reagent (prepared by dissolving 15 centigrms. of carbazol in 100 grms. of pure sulphuric acid), but in contact with nitric and hydrochloric acids it takes a red tint, as does the particular principle detected by Ader in orange-flower water; Ader's principle, however, is volatile, whilst the present pigment is fixed.

The second colouring-matter dissolves in concentrated alcohol with a yellow colour; it is not affected by nitric or hydrochloric acid, but if treated with the sulphocarbazotic reagent there appears a violet-blue colouration and then an indigo-blue precipitate.

The third pigment which we have isolated is insoluble in ethylic and methylic alcohol; it is soluble in water, to which it communicates a fine green tint. It is not affected by the acids nor by the sulphocarbazotic reagent. We have sought what may be the origin of these pigments; were they due to a transformation of principles pre-existing in natural water, or were they a secretion of living organisms? The latter hypothesis alone was verified, the distilled waters, if sterilised by Tyndall's process, having undergone no alteration, whilst check-specimens became coloured more or less strongly.

Cultures of these waters upon plates, according to Koch's procedure in various nutrient media, enabled us to isolate some chromogenic colonies.

These colonies developed the colouring-matter in certain solid media; in some liquid media they multiplied actively, but without producing chromogenic substances.

A mixture of very old distilled lettuce-water and of orange-flower water, previously sterilised, constitutes a medium in which several colonies have secreted pigment.

One of the colonies which have been cultivated gives a brownish pigment which, with hydrochloric and nitric acid, takes a reddish yellow tint, like the pigment obtained from green orange-flower water. We are inclined to consider it as a variety of Schrötter's *Micrococcus cyaneus*. The second colony which we propose to name, *Bacillus aurantii*, appears in the form of elongated cellules, grouped two by two; it is therefore a diplococcus. We have been able to cultivate it in the liquid mentioned above, to which a small quantity of asparagine had been added.

It may also develop itself in certain spoiled distilled waters; we may extract from these liquids a yellow matter, very soluble in water; its solubility has been proved by the Chamberland filter.

The pigment is precipitated from its solution by gelatinous alumina and various other reagents; it is soluble in ethylic alcohol, insoluble in methylic alcohol, and is little affected by luminous rays. To recall its origin we propose to name it *aurantio-luteine*.

The third colony contains small rods which communicate to gelatin a tint yellow by transmitted light and green by reflection. The green tint is especially manifest at the surface. The pigment dissolves in water, to which it imparts a very intense green colour. It is rather rapidly acted upon by luminous rays; it then loses its solubility; it deposits as a blackish mass, and the water becomes colourless. We purpose designating this pigment as *aurantio-chlorine*.

Lastly, a further colony has been isolated and studied. It is met in waters which are much decomposed. It liquefies gelatin, communicating to it a greenish yellow fluorescent tint. It approximates to *Bacillus fluorescens liquefaciens*.

The liquids containing these various pigments are harmless if injected into animals after sterilisation. Only the liquid, in which the last bacillus mentioned above is active, for if injected into guinea-pigs it determines a very intense inflammatory reaction and the animal ordinarily dies after a few days.

This bacillus, therefore, gives rise to a phlogogenous principle approximating to the secretion of certain pathogenic microbia described by Arloing.

These small organisms are quickly exhausted. After

two or three sowings in media which are sparingly nutritive the chromogenic properties disappear, but they reappear if the microphytes are caused to develop in stronger nutrient media.

Sometimes the chromogenic principle seems non-existent, but suddenly the liquid takes a very decided tint if we agitate it in contact with the air, or if we slightly modify its reaction.—*Comptes Rendus*, cxiv., 179.

ON THE DETERMINATION OF MOLYBDENUM.

By E. PÉCHARD.

The determination of molybdenum in the molybdates is generally effected by precipitating it in the state of sulphide, but the method gives uncertain results, on account of the difficulty encountered in weighing this sulphide. The separation and determination of molybdic acid are effected, on the contrary, without difficulty, by means of the following process.

If we pass in the cold a current of hydrochloric acid gas over an alkaline molybdate the salt becomes yellow. If we raise the temperature we see long white needles being deposited in the tube in which we operate, as observed by H. Debray (*Comptes Rendus*, vol. xlvi.), on causing hydrochloric acid to pass over molybdic acid heated to 200°. If we operate upon an alkaline molybdate heated to 440°, the separation of the acid and the base is complete, and the latter remains entirely as a chloride in the boat which contained the salt to be analysed. The white needles obtained in this operation, the composition of which has been established by H. Debray, have the formula $MoO_3 2HCl$. They are very soluble in water, and their solution, if submitted to evaporation at 100°, is decomposed, evolving hydrochloric acid, and leaving a white residue of molybdic acid, which may be at once weighed in the vessel in which the evaporation has been effected.

On operating as just described we always find a slight bluish coating deposited in the tube; it is volatile and insoluble in water. This compound is due to a partial reduction of molybdic acid, and dissolves readily on adding nitric acid to the water which serves to rinse out the tube.

This method, more easily used than the other procedures for determining molybdenum gives excellent results. It cannot be applied to ammoniacal molybdates, but their analysis is very simple. I have ascertained, in fact, that it is sufficient to heat ammonium molybdate to 440° in order to expel all the base.

Weights of ammonium molybdate equal to 2·4217 grms., and 1·5251 grms. have respectively given 1·9003 and 1·1962 grms. of molybdic acid free from ammonia. These two numbers correspond to the same proportion, 78·4 per cent of the weight of the salt taken.

In my analyses I have always taken care to attack the molybdate with hydrochloric acid at the fixed temperature of 440° to avoid the volatilisation of alkaline chloride. The molybdic hydrochlorate does not necessitate so high a temperature for its formation; it is produced in the cold, as I have been able to prove by exhausting with ether an alkaline molybdate, over which I had passed hydrochloric acid in the cold. On evaporation the ethereal solution deposits white crystals identical with those obtained by evaporating a solution of molybdic chlorhydrazine in ether.

These crystals, formed by the combination of molybdic chlorhydrazine and ether, may also be obtained very easily on exhausting with ether a mixture of concentrated hydrochloric acid and a solution of an alkaline molybdate. On evaporation the ethereal liquid deposits fine colourless crystals of the compound above mentioned.

We see, therefore, that, thanks to the production of the volatile compound $MoO_3 2HCl$, it is easy to effect an accurate analysis of the molybdates. The tungstates, too, not presenting this property, the same method is applicable to the separation of molybdic and tungstic acids in a mixture of their salts. If we cause to pass hydrochloric acid at 440° over a mixture of neutral sodium tungstate and molybdate containing 0·4664 grm. of molybdic acid, this acid is volatilised, and its weight is found = 0·4659 grm.—*Comptes Rendus*, cxiv., 173.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

(Continued from p. 79).

At one of the last meetings of the Chemical Manure Manufacturers' Association, the following exceptions were taken to the original Glaser method and the following modification adopted (H. H. B. Shepherd, Chem. News, vol. lxiii., p. 251):—

Exception Made.—(*a*) To working upon a solution representing so little as 0·4 grm. of phosphate.

(*b*). To employing nitro-hydrochloric acid as a solvent for the raw phosphate, and consequently including in the oxides of iron and aluminum any iron present in the form of pyrites.

(*c*). To the plan of dividing the phosphate of iron and aluminum found by two, to obtain the oxides instead of determining the phosphoric acid in the precipitate, and deducting this from the total.

Modified Method.—2·5 grms. of the phosphate are dissolved in 10 c.c. of hydrochloric acid and evaporated to dryness, taken up with hydrochloric acid, raised to the boiling point, washed into a 250 c.c. flask with as little water as possible, 10 c.c. of strong sulphuric acid added, and the solution allowed to stand for about five minutes with frequent shaking.

Some 95 per cent alcohol is now added, the mixture cooled, made up to the mark with alcohol, and well shaken. Owing to the contraction in volume which takes place, it must again be made up to the mark and mixed. It is now allowed to stand for one hour, filtered, 200 c.c. of the filtrate taken and gently evaporated to a small bulk in a dish. It is desirable when organic matter is present to carry the evaporation to pastiness, so that the acid may effect its partial destruction. It is then washed into a beaker with about 50 to 100 c.c. of water, boiled for a short time with a few drops of bromine or some other oxidising agent, ammonia added in excess, again boiled for half an hour, cooled, a little more ammonia added to make sure that a slight excess is present, filtered, washed with a hot solution of ammonium chloride, ignited, and weighed. Unless ammonium chloride is present, the precipitate is very apt to wash through even a very close filter. When the weight of the phosphates has been obtained, the precipitate is re-dissolved, and the phosphoric acid in it determined, the amount so found, deducted from the total weight, giving the oxides by difference. Of course, if the oxide of iron is required apart from the alumina, a separate iron determination must be made.

The following postscript was suggested by Messrs. Teschemacher and Smith:—

Should the phosphate under examination contain any magnesia, the phosphates of iron and alumina obtained in the foregoing process must be freed from this impurity by washing the precipitate from the filter and boiling with water and a little nitrate of ammonia, repeating this treatment if after first application the filtrate still shows any magnesia.

Dr. J. H. Vogel (*Zeit. f. Angew. Chem.*, 1891, xii., p.

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v. No. 12.

357) reports series of experiments made by him on the estimation of calcium by Jones's method, and on the presence of magnesia in the precipitate.

With regard to the former, he concludes that the calcium is precipitated quantitatively as sulphate, and as to the latter he makes the following statement:—

1. That when only small amounts of magnesia are present, it all passes quantitatively into the ammoniacal filtrate.

2. That with Glaser's method, as much as 3 to 3·5 per cent magnesia, and with Jones's modified method as much as 1·5 per cent may be present, there being no danger of its being precipitated with the iron and aluminum as long as care is taken to remove all the free ammonia by boiling.

3. That after the magnesia has come down with the phosphates, it will not re-dissolve on boiling, magnesium-ammonium phosphate being only sparingly soluble in hot water.

The same author has also proposed to combine the Glaser and Stutzer methods (the latter as modified by himself). If the lime is to be estimated, he advises the use of Jones's method. The alcohol is expelled from the filtrate from the calcium sulphate, the phosphates of iron and aluminum precipitated and then analysed by the modified Stutzer method. In the filtrate from the phosphates the magnesia may be thrown down by adding an excess of ammonia and allowing it to stand over night.

As I stated before, the conventional method is an unreliable one, and undoubtedly the alcohol method is a great improvement, as it has never failed to give concordant and, therefore, comparative results as applied to ordinary phosphate rocks in the hands of different chemists. Thus, where simply an approximation of the amount of iron and alumina is desired, it is of great value, the errors involved remaining very nearly constant. But when accurate work is desired, it has, as proposed, few advantages over the old method, one of the strongest objections being that of the Chemical Manure Manufacturers' Association with regard to dividing the total weights of phosphates by two, calling one-half the sum of the ferric and aluminic oxides. To eliminate the error thus introduced, we must make a phosphoric acid determination in the precipitate, and the method becomes long and tedious.

Considering the ease and rapidity with which accurate results are obtained by the molybdate method as I used it, I would prefer the latter at all times. During my work I tried the Glaser method, its modification by Jones, the combined Jones-Stutzer method as proposed by Vogel, and the molybdate method as used by Mr. McElroy.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

February 4th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MR. George German was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Meredith Wynter Blyth, 17, Marlborough Hill, N.W.; Reginald Busby Brown, Ellerslie, Knighton Park Road, Leicester; Arthur Carey, Gateacre, near Liverpool; Haridas Garjari, M.A., Agra College, Agra, India; Ernest E. Milnes, Ashfield, Bradford; Arthur Trobridge, Langley, near Birmingham.

Of the following papers those marked * were read:—

*103. "*Pedetic Motion in Relation to Colloidal Solutions.*" By WILLIAM RAMSAY, Ph.D., F.R.S.

Pedetic motion of small particles depends (1) on the size of the particles; (2) on their density; (3) on the nature of the medium in which they are suspended. An electrolyte does not cause the motion to cease at once, but the particles cohere when they happen to touch, and ultimately form clots or clusters. If an electrolyte be not present, the particles do not seem to touch. From observations with the microscope, it is calculated that a particle with a mass of $2{\cdot}8 \times 10^{-12}$ grms. moves through approximately its own diameter $1{\cdot}4 \times 10^{-4}$ c.m. in a second. Such a particle has one hundred billion times the estimated mass of a water molecule; hence, if its motion be produced by bombardment from water molecules, these must exist in complex groups of considerable mass, and of some stability. It is very unlikely that pedetic motion is the result of electric charges on the particles, because they appear to be uninfluenced by each other's motion; there is no obvious source of such electric potential; and, moreover, we know from Messrs. Linder and Picton's experiments the result of electrifying them: they are repelled from the positive or negative pole, according to their nature; but their pedetic motion is not interfered with, and is quite different in kind from the flow from the pole. An explanation of this repulsion has been given by Quincke (1861) and by Clausius (1879). The fact that pedesis is stopped by the addition of an electrolyte would appear to show that the water complices are disintegrated by the presence of ions; it may be that the individual water molecules are attracted by one or other ion, or by both.

The effect of pedetic motion in a liquid is to cause hydrostatic pressure; such hydrostatic pressure would be less on a membrane capable of penetration by the molecular aggregates or particles; and as the suspensions examined by Messrs. Linder and Picton and the colloids investigated by Graham will not pass through porous clay, they must exert pressure on its surface; the water having fairly free ingress and egress, due probably to the disintegration and the reformation of its molecular complices.

From actual observation of pedetic motion under the microscope, it cannot be doubted that the relative velocity of two particles depends on their mass; and if their volumes are approximately equal the less dense particle moves much more actively than the more dense. It would appear not in the least unlikely that equal numbers of equally sized particles would exert equal pressure, as in the case of gases.

In an article by Lothar Meyer (*Kgl. preuss. Akad. d. Wissensch.*, 1892, 26th November) on osmotic pressure, he points out the great discrepancy observed between all measurements of osmotic pressure (except those of Pfeffer on sugar), and the pressure calculated on the supposition that the space was filled with a gas at the same temperature; in all cases the observed osmotic pressure is too low, if it be supposed that ionisation occurs. There are three possibilities: (1) the so-called semi-permeable membrane acts as a sieve, and is quite impermeable to molecules over a certain volume; (2) the membrane is not impermeable, but allows molecules of different momenta to pass at different rates, as with gases of different densities and porous clay; and (3) there is combination of the dissolved substance with the membrane walls, transference through and dissociation of the compound at the interior surface of the walls, as with hydrogen and a palladium diaphragm. Tammann has shown the great probability of the truth of the last hypothesis.

I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion; that the true osmotic pressure has, probably, never been measured; and that a continuous passage can be traced between visible particles in suspension and matter in solution; that, in the words of the old adage, *Natura nihil fit per saltum.*

Discussion.

Mr. J. Y. Buchanan, having inquired whether muddy water, such as that flowing from the Rhone into the Lake of Geneva, would exhibit a higher density than the clear water when tested by a hydrometer; and Mr. Friswell having said that it was well-known it was impossible to exactly ascertain the density of oil of vitriol containing lead sulphate in suspension by means of a hydrometer, Professor Ramsay said that as particles in pedetic motion exercise pressure, they necessarily tend to force the hydrometer bulb upwards, and thus cause an apparent increase in the density of the liquid.

Referring to the stoppage of dissolved substances by partly permeable membranes, Mr. Howard pointed out that the purification of water by sand filtration had been traced to the formation of growths on the surface of the sand; when these growths reached a certain stage, however, they ceased to act.

*104. "*The Acid Action of Drawing-Paper of Different Makes.*" By W. N. Hartley, F.R.S.

In a communication to the British Association, "On the Fading of Water-Colours" (*cf.* Chem. News, vol. liv., p. 263), I showed that moisture and acidity were the chief causes of the fading of certain pigments. The acid in the air of towns is produced from sulphur in the coal, in the air of rooms from the excessive amount of gas which is burnt, and in certain colours according to their mode of preparation. It was suggested that even the slight acidity of drawing papers might be expected to facilitate chemical change, the action in each case being a gradual one. I had experimented with various kinds of the best paper in use, both of old and recent manufacture, and had come to the conclusion that such papers were invariably acid, even those of the most excellent quality. The fact was accounted for as follows:—The fibre of which the paper is made is steeped in dilute sulphuric acid, and the subsequent washing with pure water does not entirely remove the acid from linen fibre, of which the best papers are made. I have actually found fine linen to retain traces of acid after it has been steeped in frequently renewed pure distilled water for a period of three weeks. The acid seems to combine with the fibre, and the resulting compound is only slowly decomposed or dissolved by the action of water. Such linen gives a blue colour when an aqueous solution of iodine is dropped upon it. There was no intention to convey the idea that the paper contained free acid in such quantity that it could be easily removed by washing, or that it would affect *litmus paper*, which generally is not a sensitive agent. The samples of paper exhibited at the meeting were carefully tested in the following manner:—A pure and neutral solution of azolitmin, prepared from litmus, was allowed to drop upon the paper and soak into the fibres; the edges of the drops were then examined and found to be red. The bulk of the liquid was then removed by a piece of the same paper, with the result that in every case a red spot was seen which dried red. Another mode of testing was as follows:—A clear sable brush washed in distilled water was used for applying a wash of pure neutral azolitmin solution, as if it were a pigment; such washes turned red upon the paper.

Prof. Church, in his valuable work on "The Chemistry of Paints and Painting," p. 290, published in 1890, remarks that he is unable to endorse my statement that the best drawing papers have an acid action. He finds, in fact, that sized papers are generally neutral to test-papers, and that inferior papers are more often slightly alkaline than acid.

As some doubts may be entertained as to the quality of the papers examined by me, it may be well to state that they were all of the best quality, most of them being of Whatman's make. That no question may arise on this point, I have tested the samples named below in three ways: first, by dropping litmus solution upon the paper; secondly, by washing with a sable brush; thirdly, by steeping strips of paper in pure distilled warm water, and testing the water for acidity, and also for sulphates. The acid action was recognised by a pure litmus solution, by an ordinary laboratory preparation, and by a carefully prepared solution of helianthin, though this last agent is not very sensitive.

The results are identical with such as I obtained on former occasions. The description of the samples and their actions is as follows:—

1. Whatman's hand-made paper, 96 lbs., old make. Washes, acid; drops, acid; water, decidedly acid. Large precipitate with barium sulphate insoluble in dilute chlorhydric acid.

2. Whatman's double thick imperial, 140 lbs. Washes, acid; drops, acid; water, decidedly acid. Large precipitate of barium sulphate, as with No. 1.

3. Whatman's double elephant, hand-made. Washes, acid; drops, acid; water, strongly acid. Large precipitate of barium sulphate, as with No. 1.

4. Whatman's hand-made, 72 lbs., 1887. Washes, acid; drops, acid; water, decidedly acid. Large precipitate of barium sulphate, as with No. 1.

5. Saunders's hand-made. Washes, acid; drops, acid; water, decidedly acid.

6. Hollingworth's machine-made paper. Washes, barely acid; drops of strong litmus neutral in colour; water, very slightly acid, almost neutral.

7. Arnold's unbleached hand-made paper. Washes, acid.

No further tests for acidity were recorded.

All these samples were procured from Mr. Spence, Lower Sackville Street, Dublin, especially for the purpose of these tests. It will be seen from these notes that there were good grounds for attributing an acid action to even the best of drawing papers. In other words, if a very sensitive solution of pure litmus be applied to paper in the same manner as a strong pigment, as, for instance, in delicate washes, the action is, in almost every case, distinctly acid; but if a drop of a strong solution be allowed to sink into the paper and dry up, its colour may be so slightly changed as to appear violet, leading to the inference that the paper is neutral. The strength of the solution of litmus, and the manner in which it is applied, must therefore be taken into account, because the quantity of the purple colouring matter in contact with the paper may be more than sufficient to overpower the red tint caused by the acid present in the moistened material. It is therefore extremely probable that there has been no difference between the opinions of Professor Church and myself, but only an incomplete understanding as to the degree of acidity of the paper. Solutions of helianthin painted on the various samples of paper gave at first a pure yellow tint, which gradually changed to a colour intermediate between rose colour and yellow. Very dilute solutions, washed on freely, showed after some minutes a pale rose colour, mixed with a yellowish tinge. A sufficiency of acid yields a fine rose tint with such a solution. Hollingworth's paper did not show in any degree an acid action with helianthin, although it gave a slight indication with litmus.

Discussion.

Mr. Wade remarked that perhaps the sulphate detected by Professor Hartley was derived from thiosulphate, which, it was well known, was used as an antichlor in manufacturing paper.

Mr. Groves said it would be desirable to know more of the history of the papers. Was gas burnt in the room in which they were stored, and were the sheets examined taken from the tops of the packets? If so, it was possible that the sulphuric acid was derived from the gas; it would be desirable to test the centre portions of sheets taken from the middle of the packet.

Professor Hartley's remarks on this criticism are as follows:—The circumstances are not within my recollection, and I am unable to make enquiry at present, bu

drawing paper in sheets is kept in drawers, at a height of not more than three or four feet from the ground, and carefully protected from dust and damp. As a rule, the samples tested by me have been taken from the middle sheets of sketch blocks prepared from Whatman's hand-made papers, and purchased from Lechertier, Barbe, and Co., Regent Street. Imperial and double elephant were the kinds most used. I am well acquainted with the effect of a sulphurous atmosphere on paper, but cannot think that the acidity to which I refer is to be attributed to such a cause.

105. "*The Interactions Occurring in Flames.*" A Correspondence between Sir G. G. Stokes, Bart., F.R.S., and Henry E. Armstrong.

The following correspondence will serve as a contribution to the recent discussion of the chemistry of flames brought under the notice of the Society by Professor Smithells and Mr. Ingle, and by Professor Lewes. The paper referred to by Sir G. G. Stokes is entitled "On an Optical Proof of the Existence of Suspended Matter in Flames" (*cf. Proc. Roy. Soc. Edin.*, 1891). It was reproduced in *Nature*, xliv., 263, 1891.

"4, Windsor Terrace, Malahide, Ireland,
September 23, 1891.

Dear Dr. Armstrong,—I enclose a little optico-chemical paper, that is to say, one in which the method is optical, but the results are of interest, such as they have, rather from a chemical point of view. I use, to express it in short terms, a flame as a screen on which to receive an image of the sun.

The reaction mentioned in the P.S. is to be taken as a specimen of reactions of the kind, for though it probably takes place, there are doubtless others also, as there are a lot of compounds found in the interior of the flame.

I read the other day your address to the Junior Engineering Society, in which you speak of oxygen combining with hydrogen in preference to carbon; I should have supposed it would have been the other way. Not only does the facility with which steam is decomposed by glowing carbon favour this view, but it seems to me to fit better with the phenomena of flames. According to my notions, we must carefully distinguish between the changes which take place in the partial combustion of a molecule and those which are produced in neighbouring molecules as a result of the heat thus produced. We may, for the sake of a name, call the former pure chemical, and the latter thermo-chemical. The action of the heated walls of a tube is of the thermo-chemical kind; it involves a re-grouping of the existing molecules under the molecular agitation of a hot body, without bringing a fresh reagent (suppose oxygen) into play from outside the molecule. I think that in the blue base of the flame of a candle, where oxygen is plentiful, we have pure-chemical changes. The blue shell invests for a little way the highly luminous shell, like a calyx investing a corolla, and I think the thin shell of glowing carbon, to which the bulk of the light is due, owes its origin to a thermo-chemical change, the heat being derived from the combinations with oxygen which take place just outside it.

I imagine that the hydrocarbon spectrum is due to a gas formed by a pure-chemical as distinguished from a thermo-chemical change. But what gas is it? It is commonly supposed to be acetylene. To me it seems more probable that it is marsh gas, formed by a pure-chemical, not a thermo-chemical, change. According to my notion, this unknown gas (x, say) is a hydrocarbon, which when burnt without admixture of other hydrocarbons would show but feebly, if at all, the hydrocarbon spectrum. More especially might this be expected to take place if it were burnt at a reduced pressure, or considerably diluted with, say, nitrogen. For in order that x should show its spectrum its molecule must be in a state of violent agitation, which it might be expected to be if it had been born as a result of partial combustion, but would not be merely because it was going to be slain by union with oxygen.

I have not seen a statement as to the spectrum of marsh gas, as pure as may be, when burnt. Perhaps you know about it. As hydrocarbons in general (I don't know how it is as to marsh gas) show the same spectrum, x must be some gas of a simple kind formed in the process of partial combustion, though probably (at least under ordinary circumstances) itself burnt almost immediately afterwards.—Yours very truly,

G. G. Stokes."

"January 18, 1892.

Dear Sir George Stokes,—The question of the manner in which hydrocarbons are burnt, raised in your letter, has recently (on December 3rd, 1891) been brought under discussion at the Chemical Society by Professor Smithells in two papers dealing with the structure and chemistry of flames; the conclusions at which he arrives are practically identical with yours.

In making (in 1887) the statements to which you refer, I was, to a certain extent, but retailing a not uncommon opinion, although probably I was led to give prominence to the idea that hydrogen is the more combustible constituent of a hydrocarbon by the circumstance that a gas, such as methane, CH_4, yields acetylene, C_2H_2, as one of the products of its incomplete combustion; it is possible that this latter may be formed by the agency of heat alone, but I certainly am inclined to regard its production as due to partial removal of the hydrogen from CH_4, by oxygen, the more so, as Dr. Miller and I were unable to detect acetylene in oil gas manufactured by passing petroleum hydrocarbons through highly heated retorts (*cf. C. S. Trans.*, 1886, 80). Clearly, however, the case is one about which we can only reason at present; a crucial experiment which would afford a solution of the problem will not be easily devised, I think.

At the close of 1886, when my address was written, we were but beginning to realise that the phenomena of combustion are far less simple than had up to that time been taught. Had I spoken of the subject a year or two later, I should undoubtedly have adopted a less dogmatic style. Still, while admitting that the facts do not justify the assertion that oxygen combines with hydrogen in preference to carbon when a hydrocarbon is burnt with insufficient oxygen, I am unprepared at present to accept the alternative view which both you and Professor Smithells advocate, that the carbon is the more combustible; I think the actual condition of affairs is far less simple than is expressed in the statement of either of these views.

In the case of the changes attending combustion you would draw a distinction between "pure chemical" and "thermo-chemical" changes. It is impossible to deny that such a differentiation of the changes is seemingly necessary, but perhaps after all the difference is but superficial.

I cannot help thinking there is very little opportunity in flames for simple heat changes to occur; the molecules of *different kinds* are so mixed up together. Thus opportunity is given for interactions to occur, the end result of which is the same as that of a simple heat change of the chief substance concerned, merely because a change occurring at one moment is reversed the next, and so escapes notice. In this way contiguous molecules may play the part of surfaces, and that such actions are of primary importance in the case of "decompositions" as well as in the case of "compositions," there can, I think, be little doubt. Thus it appears to be established that a pure mixture of carbonic oxide and oxygen is incombustible; is it not therefore reasonable to suppose that under parallel conditions *pure* carbon dioxide is unresolvable into carbonic oxide and oxygen? Again, the results of recent experiments by Victor Meyer seem to prove that, as I have long suspected, the formation of water from hydrogen and oxygen is not the simple phenomenon it is represented to be by the simple equation $2H_2 + O_2 = 2H_2O$; and conversely it is well known that the extent to which the dissociation of water

takes place depends on the character of the surface in contact, with which it is heated, and not merely on the temperature. In fine, it seems permissible to doubt whether under the conditions prevailing in flames carbon is ever separated by simple heat changes; at all events, there is at present no evidence compelling us to conclude that it is.

Professor Smithells contends that probably carbon has a higher heat of combustion than hydrogen; this may be, but in the absence of all data from which the heats of combustion of *atomic* carbon and hydrogen can be inferred, we cannot, with safety, base any argument on thermo-chemical values. But even if it have, it does not follow that carbon is not liberated by partial combustion of hydrocarbons. It is not merely a question of the relative affinities of carbon and hydrogen for oxygen. The carbon would not, I imagine, be atomic carbon, but that complex molecular form which occurs in the flame in the solid state, and being incandescent renders it luminous. The genesis of such carbon is expressible by an equation such as—

$$xCH_4 + xO_2 = C_x + 2xH_2O.$$

Professor Smithells takes no account of the heat evolved in the formation of C_x from xC. I may also point to the superior stability at high temperatures of CO_2 as compared with CO as remarkable, seeing that it is the more complex molecule, especially as there is some ground for the belief that proportionally more heat is evolved in the fixation by carbon of the first than of the second atom of oxygen (*cf. Phil. Mag.*, [5], xxiii., 103, Feb., 1887). The probable explanation, as Berthelot has suggested, is that in this case, also, the decomposition of CO is promoted by the tendency of carbon atoms to combine.

It is also to be remembered that, although carbonic oxide as well as carbon and steam appear to interact readily enough if the temperature be sufficiently high, dry carbonic oxide and carbon do not burn in dry oxygen; nothing better illustrates the difficulty of drawing conclusions in these cases than such facts as these.

There is another point of view from which the phenomena may be regarded, from which it would seem that it is impossible to define either constituent of a hydrocarbon as the more combustible, except in a purely conventional sense. We may liken the interchanges occurring in an oxygen-methane mixture to those that occur in a cell in which two like electrodes are immersed in two different electrolytes—an aluminium acid-alkali cell, such as Wöhler (?) proposed, for example. The oxygen molecule O_2 corresponds to the aluminium, the hydrogen and carbon of the methane to the acid and alkali; and just as the aluminium is attacked in two ways, so the oxygen may conceivably become distributed between the carbon and hydrogen. The formation of the two aluminium compounds is independent of the relative affinity to aluminium of the radicles of the acid and alkali, and in like manner that of the two oxides from methane would be conditioned by the orientation of the oxygen atoms relatively to the carbon and hydrogen atoms of the hydrocarbon; for we may assume, I think, that the colliding oxygen and hydrocarbon molecules conjugate if only during a very brief interval of time, and that interaction is indeed a consequence of the opportunity thus given to the atoms to re-group themselves.

There appears to be no doubt that surfaces of various kinds—I would even include gaseous surfaces—play an all-important part in promoting all kinds of *reversible* changes; but it is a fair question for discussion whether their action is not also of a "pure chemical" character. The fact that the nature of the surface is of moment is in favour of the view that it is—the surface must be a *compatible* one: the separation of hydrogen from a hydrogen compound being especially promoted by platinum, which undoubtedly has a strong affinity for hydrogen, and that of oxygen being promoted by silver, which, at high temperatures, is known to absorb this gas. On the other hand, copper, although so readily oxidisable, does not appear to promote the decomposition of water. Even in such a case as that of the dissociation of carbon dioxide by red hot porcelain, it is conceivable that the porcelain may exert an attraction over atomic oxygen sufficient to induce its separation from carbon. I, therefore, am not satisfied that the action of the heated walls of a tube is, as you suggest, strictly of the thermo-chemical kind.

There is a striking passage in Faraday's paper on the influence of platinum in promoting the interaction of hydrogen and oxygen (*Exp. Res.*, Series VI., paragraph 656, November, 1833), which shows that he had clearly realised how important is the influence of surface action even in the case of flames. He says:—

'I have pursued this subject at some length as one of great consequence, because I am convinced that the superficial actions of matter, whether between two bodies or of one piece of the same body, and the actions of particles not directly or strongly in combination are becoming daily more and more important to our theories of chemical as well as of mechanical philosophy. In all ordinary cases of combustion it is evident that an action of the kind considered, occurring upon the surface of the carbon in the fire, and also in the bright part of a flame, must have great influence over the combination there taking place.'

Regarding the interactions in flames as consisting in a series of simultaneous and consecutive explosions, of which we can only examine the final steady state, it seems to me that the phenomena are necessarily of an excessively complex character, and that their appreciation and successful interpretation must tax our powers of mental analysis in a very high degree. It will certainly be unwise at present to infer that the oxidation of the hydrocarbons, or the separation of carbon and also of hydrogen from them, takes place entirely in any one way.—Yours very truly,

Henry E. Armstrong."

"21st January, 1892.

Dear Professor Armstrong,—Perhaps I may be allowed to add a few words in explanation of what I meant by thermo-chemical change. I had not in view thermic measurements. I will endeavour to explain my ideas by an example. Let us contrast (*a*) the formation of water from mixed oxygen and hydrogen, (*b*) the formation of acetylene and hydrogen from marsh-gas at a high temperature. In both cases alike molecular agitation is required to bring about the change; in (*a*) if the change be brought about at one point, the consequent agitation supplies the requisite disturbance to the neighbouring molecules, and the change is propagated with explosions; but in (*b*) I picture to my own mind the change as taking place in this way. When sufficient heat is supplied to the gas from without, the collisions of the molecules of the marsh-gas become sufficiently violent to allow the carbon atoms in a pair to get into a condition in which their tendency to self-combination comes into play, and in the coalescing a portion of the total hydrogen in the pair is thrown off. But the continuance of this change is dependent on a continuous supply of heat from without, under which it is gradually effected. I should call (*a*) a pure-chemical change, even though heat at one point is necessary to start it, and I should call (*b*) thermo-chemical, even though chemical affinities are concerned in it.

The results of Prof. Smithells seem to me to make it probable that x may be carbonic oxide.—Yours very truly,

G. G. Stokes."

106. "*Properties of Alcoholic and other Solutions of Mercuric and other Chlorides.*" By S. Skinner, M.A.

The author has determined the variation in the boiling-point of alcohol produced by dissolving in it mercuric, lithium, magnesium, and calcium chlorides, as well as the variation in the boiling-point of a solution of hydrogen

chloride of constant boiling-point produced by mercuric chloride. He has also studied the distribution of mercuric chloride between the two solvents water and ether.

The results indicate that mercuric chloride affords a case in which the measure of the property is a simple function of the quantity of salt present, whereas in the case of the other chlorides the measure of the property involves some higher power.

107. "*The Isomeric α-Bromocinnamic Acids.*" By S. Ruhemann, Ph.D., M.A.

An account is given of experiments on the action of ammonia and phenylhydrazine on the ethereal salts of the two isomeric bromo-acids obtained on withdrawal of hydrogen bromide from dibromhydrocinnamic acid. Whereas the ethylic salt of α-bromocinnamic acid and ammonia readily interact, yielding α-bromocinnamonamide, the α-isocinnamate is scarcely affected by ammonia.

Both salts are converted by phenylhydrazine into a compound of the formula $C_{15}H_{11}N_3O$, the change taking place less readily in the case of the iso-salt. The author regards this product as cinnamylphenylazimide; the same substanee is more readily prepared by interaction of ethylic dibromhydrocinnamate and phenylhydrazine. In both cases the yield of azimide is but small, the main product being a compound of the formula $C_{24}H_{18}N_4O_2$, probably the imide of dicinnamylphenylazimide. The author discusses the manner in which this compound is formed.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—Mr. Groves (Chem. News, vol. lxv., p. 84) says that the circular issued by the Association of which I am the Honorary Secretary gives a garbled quotation from the Charter, in stating that the Institute was founded for the elevation of "analytical chemists," instead of "*consulting and* analytical chemists." Mr. Groves has taken an uncharitable view of that omission, for I find on referring to the original copy sent to the printer that the words are correctly quoted; but the printer, unfortunately, omitted the word "consulting," and I had not time to revise the proof as carefully as I should have wished. The omission, however, of the word "consulting" rather detracts than otherwise from the strength of the position taken by the Association.

The Institute was founded for the elevation and regulation of persons in practice as consulting and analytical chemists, and not for those engaged as professors of, or lecturers on, chemistry. It is obvious, however, that we have many brilliant chemists amongst the professors and lecturers, and everyone will agree that the views of those gentlemen should receive the most careful consideration. Chemists engaged in works ought also to have a large measure of influence in the management of the affairs of the Institute. But, according to the Charter, the Institute was founded mainly for the elevation of consulting and analytical chemists, in order to give to them a higher position, by reason of their being recognised as qualified, and the public greater assurance as to their qualifications. Under these circumstances surely the managing body should consist mainly of members who are in active practice as consulting and analytical chemists.

Mr. Groves asserts that no pledge was given to publish a *full* report of the proceedings of the Conferences of the Institute. Those who were present at the May meeting will no doubt remember that Mr. Groves *stated* that it was intended to publish full reports for the benefit of members who could not attend the proceedings of the Conference. Shorthand notes were taken for that purpose, and the transcript of remarks which I made was forwarded to me for correction. This I revised and returned to Mr. Groves, and I was subsequently informed, after the papers and discussions were in print, that the Publication Committee had resolved not to circulate them amongst the members of the Institute. But the circular referring to the December Conference, which Mr. Groves cites, says: "A *full* report of the proceedings will not be published." Will Mr. Groves say that a report of any kind whatever, either full or otherwise, has been or will be published? And if not, will he say that the pledge that a report of some kind would be published has not been broken?

The chief object of our Association is to obtain better representation on the Council of the Institute by members who are in active practice as consulting and analytical chemists, and I have received many replies from professors of, and lecturers on, chemistry who think this is a fair thing to ask. There is no breach between consulting and analytical chemists on the one hand and teachers of chemistry on the other, so far as I know.

I am sorry Mr. Groves wrote the last paragraph of his letter, because it insinuates sinister motives on the part of gentlemen who, no one could doubt, would fully uphold the integrity and dignity of the Institute.

Mr. Groves requests the members not to hand over the Institute bound hand and foot to the public analysts, "or rather to a small and noisy party of progress (?), who form but an exceedingly small fraction of the large body of professional chemists." It must be evident to Mr. Groves, although *we* do not make any such assertion, that we might with equal justice say that it at present lies bound hand and foot under the dictation of a small body of lecturers on chemistry, who form a still smaller section of the whole body of the Institute. We have too much respect for all the members nominated on the proposed Council to make such an assertion, and are content to place our views before the Institute, which we have done by a circular addressed to each member, and to leave the decision with them. If they think that members in active practice as consulting and analytical chemists should form at least half the number of the governing body, I trust they will vote for the list we shall propose to them. If they do not hold these views, they will no doubt vote against us, and Mr. Groves will find by the result which views are the more acceptable to members.

It is specially provided by the Charter that alterations in the Council may be made every year by the members, and I trust that Mr. Groves will not try to imbue them with the erroneous notion that they have no moral right to make use of that provision to express their views. If the action of the Council so elected be not pleasing to the majority of the members, the same provision will enable them next year to alter the Council as they think fit. The Council is to the Institute what the House of Commons is to the Nation. The majority of the Council corresponds to the supporters of the Government, and if their policy is distasteful to the general body of members it is strictly within the province of the latter to replace them by men who will better represent their views.—I am, &c.,

William Thomson.

Manchester, Feb. 13, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—As one of the fifty-nine members of the Institute of Chemistry who signed the circular to which Mr. C. R. Groves takes exception in his letter published on p. 84, I desire to say that Mr. Groves is quite right in his belief that neither Mr. W. Thomson, myself, nor any of our co-signatories would have consented to their names being attached to a document which they knew contained

garbled quotations or untrue statements. In fact, the names appended to the circular include those of men in the first rank and all branches of their profession, representing every part of the kingdom. That these gentlemen have formed an association and appealed to their brother chemists to adopt proper constitutional means to effect a change in the management of the affairs of the Institute, is at once a proof that reform is urgently required, and a guarantee that the agitation will be conducted with fairness, frankness, and moderation.

How the words "and consulting" came to be omitted from a sentence purporting to be quoted from the Charter I do not know, but Mr. Groves' suggestion that the omission was designed is clearly untenable. The whole gist of the circular evidently is that the interests of the Institute have suffered and its objects been imperfectly attained through the consulting and analytical chemists in active practice not being adequately represented on the Council; and the policy of the Association is clearly set forth as being to secure the election on the new Council of a majority of those coming under this designation.

As Mr. Groves takes upon himself to correct certain statements in the circular, he should, at least, take care that his own allegations are not open to exception. Thus he describes the fifty-nine signatories as "some fifty members of the Institute, nearly all public analysts," whereas I can only count some fifteen or sixteen (or 25 per cent), as holding public analysts' appointments. Among the remainder I recognise the names of professors and lecturers on chemistry, consulting and analytical chemists, pharmaceutical chemists, works managers and chemists, medical men, &c.

But Mr. Groves is guilty of a still less excusable inaccuracy, and one which, coming from him, somewhat surprises me. He asserts that the statement in the circular that "a distinct pledge was given that the papers and discussions of last year's conferences should be published" is, "to speak quite plainly, untrue." So far from being "untrue," *I myself, with scores of others, heard Mr. Groves state* that the papers and discussions at the May Conference would be published in full. This promise was given by Mr. Groves in open meeting, in reply to a direct question as to the intentions of the Council. Further, a shorthand writer attended and took verbatim notes of the discussions. These were afterwards transcribed, and I duly corrected and returned to Mr. Groves the report of my own share in the discussions.

Proceedings in Council are generally held to be more or less confidential, but it is an open secret, which, I presume, will become generally known on publication of the balance-sheet, that the papers and discussions were duly printed at a *cost of upwards of fifty pounds!* I did my best to induce the Council to publish the reports of the May Conference, and believe if this had been done it would have furnished a safety-valve for the rapidly growing dissatisfaction with the past policy of the Council, and probably have prevented the present action of the members.

While Mr. Groves gave a definite promise that a full report of the May Conference should be published, it is quite true that it was announced that no *full* report would be published of the Conference held in Christmas week; which decision was undoubtedly wise, bearing in mind the eminently inconvenient date chosen for the meeting, and the broken pledge respecting the proceedings at the previous Conference.

I may say that personally I greatly regret that such a course as that which members are now taking should have been rendered necessary; but my experience in the Council of the Institute has convinced me that no good can be expected without such a change in its policy as can only be effected by placing on it a working majority of those actively interested in the primary object for which the Institute was founded; which, as defined by the Charter, is "the elevation of the profession of consulting and analytical chemistry, and the promotion of the efficiency and usefulness of persons practising the same, by compelling the observance of strict rules of membership and by setting up a high standard of scientific and practical proficiency." If repeated disappointments had not convinced me of the hopelessness of attempts at reform from within the present and proposed Council, I should not have joined the Association, and in taking that step I am in no way animated by personal feeling or want of good will towards those members of the Council whom I hope the supporters of the Association will succeed in replacing by men more directly representative of those branches of the profession which I hold should constitute the majority.

Whatever may be the divergence in our views, I presume that all are acting in what they believe to be the best interests of the Institute, and hence I deprecate such sneers as those indulged in by Mr. Groves. They merely serve to accentuate the unfortunate differences between the various branches of the profession, while affording to neutral men a clue to the spirit and policy which have brought about the present lamentable condition of things. It is always painful to disagree with one's personal friends, and I am proud to be able to count many of these in every branch of the profession; but I fail to see that the matters at issue justify the adoption of such a tone as that of which Mr. Groves makes himself the mouthpiece.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, February, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The circular against which the wrath of the late Secretary of the Institute of Chemistry is directed was signed by 59 members of the Institute. According to Mr. Groves these are nearly all Public Analysts who are trying to hand over the Institute bound hand and foot to their own body.

As the President of the Society of Public Analysts, I am bound to show that this allegation is entirely unwarranted. Of the 59 signatories only 16 are Consulting and Analytical Chemists holding appointments as Public Analysts. The movement is therefore wrongly designated a Public Analyst movement. It is one of Analytical and Consulting Chemists against the usurpation of their rights, as expressed by the Charter of the Institute, by a certain number of chemists whose interest in the Institute is merely of a secondary character. Mr. Groves should recognise that the majority of those who have signed the circular have as much right to the designation of Consulting Chemist as he himself has.

It is idle to call the party who are now once more attempting to guide the Institute upon the strength of the charter into constitutional lines, "a small and noisy one," "who form but an exceedingly small fraction of the large body of professional chemists." There is an equally noisy fraction among the party that has so long been in power with disastrous results. The ballot at the annual meeting will, I believe, disagreeably surprise the late secretary.

As a late member of Council I desire to add that Mr. Groves must surely know that the conferences of the Institute were started with the full intention on the part of the Council to publish the papers and discussions. The matter was at great length before the Council, and it was well understood that the publication should, if possible, be the means of showing to the Fellows that the Institute was not so inactive and useless as was largely believed. Only when it was found that the discussions and papers were distinctly hostile to the past policy of the Council, and after the papers read and the discussion at the first conference were in type, did the Council alter its former intention and relapse into its policy of silence.

This is fresh in the recollection of many of those who, like myself, were members of the Council at the time the conferences were resolved upon. Whether there is any *documentary* evidence of the fact is beside the point, for surely Mr. Groves does not intend to distinguish between his *word* and his *bond*.—I am, &c.,

OTTO HEHNER.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

SIR,—Some college students have recently formed a scientific society for their general benefit and the furtherance of their chemical knowledge. Now the students have the difficulty (which no doubt you once experienced yourself), in selecting the branch of chemistry they should follow. I am therefore requested to ask for opinions on that subject.

The question then is, should a young chemist take up the teaching of chemistry, or should he take it up with a view to a future position as public analyst? or, again, should he go into a works as an analytical chemist? If the latter, what branch in particular would you recommend to anyone who has a wish for future advancement, and *also* has some enthusiasm for the science?—I am, &c.,

W. S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 5, February 1, 1892.

Compressibility of Saline Solutions.—Henri Gilbault.—The author has essentially followed the method adopted by Cailletet, and he has formulated twelve laws.

Barium and Strontium Nitrides.—M. Maquenne.—On passing a current of nitrogen at a red heat over an amalgam of barium, strontium, or calcium, placed in a boat of iron and nickel, we obtain a mixture of alkalino-earthy nitride with a slight excess of the corresponding metal, particles of finely divided iron or nickel, a little mercury, and lastly a trace of baryta, strontia, or lime. The quantity of hydrogen given off on treating this mixture with water varied greatly. Barium and strontium nitrides have the same constitution as magnesium nitride, Ba=N—Ba—N=Ba, which recalls immediately that of triethylene diamine. Barium nitride does not yield ethylated bases with alcohol. At a red heat it fixes energetically carbon monoxide, and is thus converted into a mixture of baryta and barium cyanide. Lithium is also capable of rapidly absorbing nitrogen, thus presenting a new analogy between this metal and those of the magnesium family.

On Carbon Chlorobromides.—A. Besson.—Theory indicates the probable existence of three carbon chlorobromides of the type CX_4, *i.e.*, CCl_3Br, CCl_2Br_2, $CClBr_3$. The first mentioned was obtained by Friedel and Silva by the action of bromine upon chloroform at 170° in sealed tubes. The author has tried this reaction at a higher temperature, and has obtained simultaneously all the three chlorobromides.

Action of Metals upon Salts dissolved in Organic Liquids.—Raoul Varet.—Certain metals, capable of precipitating other of their salts dissolved in water, lose this property if for water we substitute certain organic liquids; this difference is due sometimes to the water and sometimes to the action of molecular compounds created by the union of the products present.

Monosodium Mannite.—M. de Forcrand.—A thermochemical paper, not suitable for abstraction.

Conversion in the Animal Economy of Sulphanilic Acid into Sulphanilocarbamic Acid.—J. Ville.—Sulphanilic acid, in its passage through the economy, undergoes a modification analogous to that observed by Salkowski in taurine. The acid amine is converted partially into uramic acid and sulphanilocarbamic acid, which is eliminated in urine.

Chemical Study of the Chlorophyllic Substances of the Pericarp of the Grape.—A. Etard.—There exists in the chlorophyllic bodies of the pericarp of the grape a considerable quantity of palmitic acid, partly combined with a substance having a high molecule, and which, doubtless, easily adapts itself to the transformations of organic life on account of the mobility of its properties of hydration.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 11.

Solution of Bismuth Chloride in Saturated Solutions of Ammonium and Sodium Chlorides and on Bismuth Salicylates.—H. Causse.—The author has observed that certain chlorides, especially those of ammonium and sodium, prevent the dissociation of the bismuth and antimony salts by water. He has applied his researches to the preparation of the neutral and the basic bismuth salicylates.

Action of Capryl Iodide upon Trimethylaniline in Aqueous Solutions, Hot, and in Equimolecular Proportions. Formation of Free Dimethylcaprylamine of Tetramethylammonium Iodide, of Trimethylamine Hydriodate, and of Caprylene.—H. and A. Malbot.—The author's results are: dimethylcaprylamine is formed according to the reaction—

$$N(CH_3)_3 + IC_8H_{17} = N(CH_3)_2H_{17} + ICH_3.$$

Tetramethylammonium iodide results from the union of the trimethylamine which remains available to the methyl iodide formed in the first reaction.

Series 3, Vol. vi., No. 12.

On Codeine Violet.—P. Cazeneuve.—Already noticed.

Determination of Creatinine in Urine.—J. Moitessier.—Already inserted.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Medical, 8.30.
TUESDAY, 23rd.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Society of Arts, 8. "Artistic Treatment of Jewellery—Jewel and Address Caskets," by Mr. J. William Tonks.
WEDNESDAY, 24th.—Society of Arts, 8. "Ancient and Modern Art Pottery of Japan," by Ernest Hart.
—— Geological, 8.
THURSDAY, 25th.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Some Recent Biological Discoveries," by Prof. E. Ray Lankester, M.A.
FRIDAY, 26th.—Royal Institution, 9. "On Optical Projection," by Sir David Salomons, M.A.
—— Physical, 5. "On Modes of Representing Electromotive Forces and Currents in Diagrams," by Prof. S. P. Thompson, F.R.S. "On the Flexure of Long Pillars Under their Own Weight," by Prof. M. FitzGerald, M.A. "On Choking Coils," by Prof. J. Perry, F.R.S.
SATURDAY, 27th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

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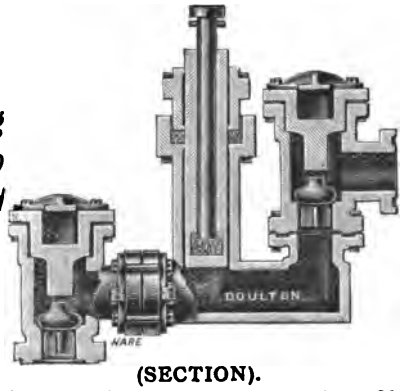

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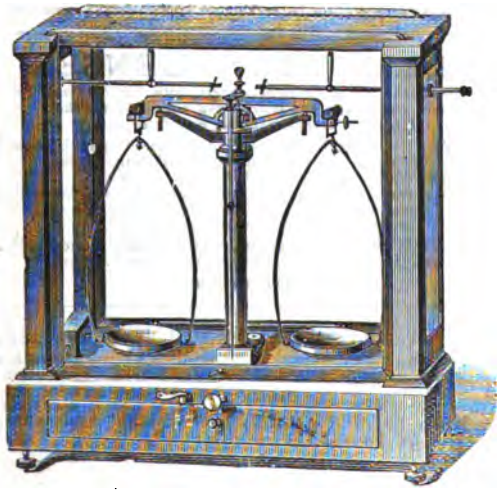

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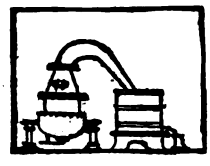

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THE CHEMICAL NEWS.

Vol. LXV., No. 1683.

THE SPECIFIC HEAT OF ALUMINIUM.*

By J. W. RICHARDS, Lehigh University.

The determinations of the specific heat of aluminium are but few in number, and yet vary widely.

As soon as Sainte-Claire Deville had obtained a button of aluminium in 1855, his friend Regnault importuned him for a specimen with which to determine its specific heat, and although Deville knew that the metal he had made was far from pure, yet he yielded to Regnault's request and furnished him with three small pieces, which analysed—

Silicon	2·87
Iron	2·40
Copper	6·38
Lead	traces
Aluminium	88·35

Regnault determined the mean specific heat of this metal between 25° and 97° to be 0·2056. He attempted to calculate approximately the specific heat of pure aluminium by allowing for the impurities present. In doing this he assumed the specific heat of silicon to be 0·1425, it not having been then determined, and his calculation gave him 0·2181 as the number for pure aluminium. Had he, however, used what we now know to be the specific heat of silicon, 0·21, he would have calculated 0·2200 as the specific heat of pure aluminium between 25° and 97°.

A year later Regnault obtained aluminium about 97 per cent pure. He obtained for this, between 14 and 97°, 0·2122. Allowing for the impurities present, he calculated 0·2143 as the probable number for pure aluminium.

It may be remarked in passing, as a curious fact, that Regnault treats these mean values as if they were invariable constants, independent of the range of temperature through which they were determined.

Following Regnault came Kopp, who in 1863 made determinations with ordinary Parisian aluminium. He obtained 0·2020 as the mean value between 20° and 52°. However, no analysis is given of the metal used, and from a consideration of the way in which Kopp experimented, and the degree of accuracy which was possible in his experiments, it is evident that his results are of very little value. For instance, four determinations gave him—

0·1970
0·2000
0·2070
0·2020,

from which he simply deduces 0·2020 as an average value.

In 1882, Professor Mallet made some absolutely pure aluminium for his researches on the atomic weight, and he determined its mean specific heat between 0° and 100°, by means of a Bunsen ice calorimeter, to be 0·2253. Since no impurity was present in the metal, this determination is free from one of the sources of error of the previous ones.

More recently, Naccari, the noted Italian physicist, states that he obtains for the true specific heat of aluminium at various temperatures the following values:—

18°	50°	100°	200°	300°
0·2135	0·2164	0·2211	0·2306	0·2401

It will be noticed that these values indicate that the specific heat increases 0·0095 per 100°, and lead to the formulæ—

$$S = 0.2116 + 0.000095\,t$$
$$Sm = 0.2116 + 0.0000475\,(t_2 + t_2),$$

in which 0·2116 is the true specific heat at 0°. The mean between 0° and 100° would be 0·2164, comparing well with Regnault's results, but much lower than Mallet's. It is not stated what was the purity of the metal used by Naccari.

The question which the writer set out to solve presented itself to him in this way: Who is nearest the truth, Regnault and Naccari, or Mallet?

I obtained some aluminium made by the Hall process, which analysed—

Silicon	0·07
Iron	trace
Aluminium	99·93

Since the atomic weight of silicon is almost identical with that of aluminium, it was felt safe to neglect the influence of the 0·07 per cent present.

Three methods of procedure were used. First, a large weight of aluminium (100—200 grms.) was put into an empty calorimeter, whose water equivalent had been accurately determined by experiment, and allowed to stand several hours. When the temperature was nearly constant, a known weight of water at a higher temperature was run in, and the total loss of heat calculated from the observations. This method gave mean specific heats between about 16° and 22°. Secondly, the aluminium was suspended in steam and dropped into the water in a colorimeter. This gave values from 20° to 100°. Thirdly, two exactly similar calorimeters were used. The aluminium and a platinum ball weighing 52 grms. were placed on a platinum support and heated together either in an air-bath to 120°, or in a small furnace up to 400°, 500°, and 600°. The platinum ball was dropped into one calorimeter and the lump of aluminium into another. From the heat given out by the platinum its temperature was calculated, and assuming that the aluminium had been at the same temperature, I had the data for calculating its mean specific heat.

The third method gave the most concordant results. The first method was used for such a small range of temperature that the experimental errors were large. The second method was defective in default of suitable apparatus to secure the instant transfer of the metal from the steam into the calorimeter. The third method had the advantage, that since the platinum and aluminium were taken out of the furnace together and were dropped almost simultaneously into the calorimeters, it could fairly be assumed that they would cool about the same amount in the two or three seconds during which they were exposed to the air.

The writer has made two experiments by the first method, five by the second, and sixteen by the third. Selecting those experiments which were experimentally the nearest to perfect ones, and correlating the data by the method of least squares, the following formulæ were arrived at:—

$$Sm = 0.2220 + 0.00005\,(t_1 + t_2)$$
$$S = 0.2220 + 0.0001\,t,$$

in which 0·2220 is the true specific heat at 0° C.

From these formulæ the following values will be shown:—

Temperature.	True Specific Heat.	Range of Temperature.	Mean Specific Heat.
0°	0·2220	0°—100°	0·2270
20°	0·2240		
100°	0·2320		
		0°—625° (melting-point)	0·2533
625° (melting-point)	0·2845		
		Total caloric capacity to the m.p.	158·3

* Read at the Chemical Section of the Franklin Institute, December 15, 1891.

It is seen that the author's results confirm Mallet's determination, as far as the true specific heat is concerned, and agree closely with Naccari's observation of its rate of increase with the temperature.

Atomic heat,—

$$0{\cdot}2270 \times 27{\cdot}02 = 6{\cdot}13,$$

using the mean specific heat between 0° and 100°, as is done with almost all other metals.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

(Concluded from p. 90).

Experiments on the Glaser Method.

In the first estimations made by this method I noticed, when the alcohol was evaporated, the formation of crystals of calcium sulphate, and therefore discarded it, as these crystals would contaminate the phosphate precipitate.

Experiments on Jones's Method.

This method separated the calcium perfectly. In boiling off the alcohol I noticed the formation of aldehyd, which was accompanied by a reduction of the iron. It is therefore necessary before adding the ammonia to boil for a few moments with a few drops of nitric acid. Jones claims that the calcium is separated quantitatively, and that the alcohol is diluted sufficiently by the water present to keep the bases in solution. While working with this method I noticed that the ignited calcium sulphate was invariably slighly rose-coloured. Upon investigation I found this to be due to small quantities of iron, which were precipitated by the alcohol. I then tried to remove this by continued washing of the freshly precipitated calcium sulphate, but even after using a litre of 85 per cent alcohol I still found the calcium sulphate contaminated with iron. Here then there is a grave source of error which is no doubt due to the large quantity of alcohol used, as I never observed any iron in the calcium sulphate obtained by Glaser's method. Through lack of time I did not determine the quantities of iron thus taken down; but they were considerable, and increased with the percentage present in the original substance.

I was here curious to investigate the action of potassium and ammonium salts on the precipitation of the calcium, and my work led me to some astonishing results.

Four solutions were made as follows:—

1. An unknown solution of calcium phosphate, the latter being brought into solution by means of a little hydrochloric acid.
2. A solution of potassium chloride containing 1·0 grm. in 100 c.c.
3. A solution of ferric chloride containing 0·22 grm. Fe_2O_3 in 10 c.c.
4. A solution of ammonium chloride containing 1·0 grm. in 100 c.c.

The calcium was precipitated according to Jones. It was first estimated in the calcium phosphate solution, 25 c.c. being used with 10 c.c. of the ferric chloride solution.

Two estimations gave calcium sulphate:—

0·2519 grm.
0·2519 „

These agree exactly, but both were slightly rose-coloured. A mixture was then made of 25 c.c. of calcium solution, 10 c.c. of the iron solution, and 5 c.c. of the potassium chloride solution. Two estimations gave calcium sulphate:—

0·2785 grm.
0·2784 „

Both of these were highly coloured with iron, and a qualitative examination revealed the presence of potassium.

Then 25 c.c. of the calcium solution, 10 c.c. of the iron solution, and 10 c.c. of the potassium chloride solution were mixed, and the calcium separated and weighed.

Two estimations gave calcium sulphate:—

0·2805 grm.
0·2800 „

These two contained still more iron, and potassium was again present.

The influence of the ammonium chloride was then tried. I again used 25 c.c. of the calcium solution, 10 c.c. of the iron solution, and 5 c.c. of the ammonium chloride solution.

Two estimations gave calcium sulphate:—

0·2541 grm.
0·2543 „

and on using the same mixture with 10 c.c. of the ammonium chloride solution, I obtained calcium sulphate:—

0·2563 grm.

It thus appears that the presence of potash and ammonium salts increases the amount of iron present in the calcium sulphate. The presence of the alkali shows that the alcohol precipitates it and the iron as double sulphates or alums which are much less soluble in alcohol than any other ferric and aluminic salts.

Ammonium salts do not exercise this influence to so great an extent as potassium salts, but still sufficiently to vitiate the subsequent results. This renders the Jones method inapplicable in cases where these alkalies are present, as in soils and ashes, and the presence of small quantities of iron, even in those instances where no alkali was added, indicates that the quantity of alcohol prescribed by Jones is too high.

It is of interest to note the manner in which the presence of potassium or ammonium salts influenced the form in which calcium sulphate precipitated. Usually when the alcohol is added the precipitate in a very short time becomes crystalline. When these salts, however, are present, it precipitates in a flocculent form, and remains so, even if allowed to stand over night.

Finding in this manner possibilities of error which rendered both methods doubtful, I decided to try the Stutzer method as modified by Vogel, with previous removal of the calcium, according to Glaser's directions. In two other portions of the solution the calcium was precipitated according to Jones.

I append the results obtained with a phosphate rock:—

Sample.	Method.	Weight material. Grm.	Weight precipitate.	Per cent combined oxide.
1 ..	Glaser-Stutzer.	0·500	0·0085	1·70
1 ..	„	0·500	0·0084	1·68
1 ..	Jones-Stutzer.	0·500	0·0028	0·56
1 ..	„	0·500	0·0032	0·64

We see that much less iron and aluminum was present in the alcoholic filtrate obtained by Jones's method, and this is another proof that some of it is retained by the calcium sulphate.

I now turned to the molybdate method used by Mr. McElroy, it appearing that this should, if properly and carefully carried out, give accurate results. On a preceding page I have given a description of this method. It is necessary to resort to a double precipitation of the hydrates, as when the ammonia is first added a small amount of molybdic anhydride is liable to separate out in the form of a white powder. If the liquid is kept as cool

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 12.

as possible and the ammonia added only in slight excess, this is reduced to a mininum. It never occurs in the second precipitation.

The method was tried on four phosphate rocks and gave the following results:—

Sample.	Weight material.	Weight precipitates.	Per cent oxides.
1	0·200 grm.	0·0052	2·60
1	0·200 ,,	0·0053	2·65
2	0·200 ,,	0·0022	1·10
2	0·200 ,,	0·0021	1·05
3	0·200 ,,	0·0064	3·20
3	0·200 ,,	0·0068	3·40
4	0·200 ,,	0·0099	4·95
4	0·200 ,,	0·0100	5·00

Sample 1 is the same as that to which the Stutzer method was applied, and we see that the molybdate method gives much higher results, which from the nature of the method are undoubtedly much more accurate.

This method was tried with success in the analysis of soils by Mr. J. L. Fuelling. By permission I include some of his results.

Sample.	Per cent oxides.	Sample.	Per cent oxides.
a	2·32	*c*	1·19
a	2·26	*c*	1·19
b	1·48	*d*	1·23
b	1·55	*d*	1·23

The greatest deviation between duplicates, we see, is 0·07 per cent, an allowable difference which occurs in all analytical work.

All in all, the above shows that this method is to be preferred to all others, being as short and as rapid as the alcohol method, giving more accurate and concordant results, and giving the oxides in a form which is easily rendered soluble, so that the iron can be accurately estimated.

REPORT ON DETERMINATION OF NITROGEN.*

By E. B. VOORHEES.

As your reporter on nitrogen, I now have the honour to present the results of the work done by the Association this year. As far as your reporter has been able to review the foreign and American journals, he has not found that the past year has developed any particularly new or desirable additions to our present official methods. The Report, therefore, will include chiefly (1) the results secured by members of the Association, and (2) recommendations and suggestions.

Early in the year a circular letter asking co-operation in the work of the Association was sent to all chemists connected with experiment stations, to seven commercial chemists, and to such others as were so entitled by our constitution, numbering in all about forty. Thirty-two, representing twenty-six stations, the United States Department of Agriculture, and that of Virginia, and five commercial chemists, signified their desire to take part in the work. Three samples were sent to each of these early in March, accompanied by another circular letter, asking that a moisture determination be made in each of the samples, and that the nitrogen determination be made according to the official and alternate methods. The Report for 1889 had not then been distributed, hence they were asked to use those methods described in the Report of the Association for 1888, with such additional modifications as were recommended by the reporter in 1889. The samples were marked 1, 2, and 3, and were made up as follows:—

Description of samples.	Per cent nitrogen.	Grms.
No. 1.—Potassium nitrate containing ..	13·72	400
Sodium nitrate containing	16·14	56
Calculated per cent of nitrogen	14·01	
No. 2.—Linseed meal containing	7·15	250
Cotton-seed meal containing ..	5·50	250
Sodium nitrate containing	16·14	100
Calculated per cent of nitrogen	7·96	
No. 3.—Dried blood containing..	13·92	300
Ammonite containing	13·02	300
Calculated per cent of nitrogen	13·47	

The Report includes the work of twenty-four chemists, representing but fourteen of the twenty-five experiment stations which early in the season desired to co-operate, and the departments of agriculture of the United States and of Virginia. No commercial chemists are represented.

Results.

The percentage of moisture was not reported by all of the chemists, and since the amounts reported in samples 1 and 3 were very uniform, all results are based upon original substance. The method of standardising the acid was mentioned in only three reports; in these the tetraoxalate was used with good results.

Kjeldahl Modified for Nitrates.

Analysts.	Per cent nitrogen. No. 1.	No. 2.
Walker Bowman (Virginia Experiment Station)..	13·95	7·49
R. C. Kedzie (Michigan Experiment Station)..	14·04	8·40
H. R. Baldwin (West Virginia Experiment Station)	13·73	7·88
F. B. Carpenter (North Carolina Experiment Station)	13·76	7·36
H. J. Patterson (Maryland Experiment Station)..	13·82	7·66
B. F. Finney (Virginia Experiment Station)..	13·86	7·77
R. H. Gaines (Virginia Department of Agriculture)	14·13	7·68
T. C. Trescot (United States Department of Agriculture)	13·40	7·65
J. M. Bartlett (Maine Experiment Station)..	14·12	7·64
L. H. Merrill (Maine Experiment Station)	14·20	7·74
W. H. Beal (Massachusetts Experiment Station)..	13·80	7·61
F. W. Morse (New Hampshire Experiment Station)	14·13	8·04
C. L. Parsons (New Hampshire Experiment Station)	14·05	7·79
C. D. Woods (Stoors Experiment Station)	14·04	7·97
Duncan Adriance (Texas Experiment Station)..	13·79	
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	13·74	7·74
L. A. Voorhees and C. S. Cathcart (New Jersey Experiment Station)	14·04	7·94
B. B. Ross (Louisiana Experiment Station)..	14·11	7·87
G. L. Holter (Pennsylvania Experiment Station)..	13·45	7·81
M. A. Scovell (Kentucky Experiment Station)..	14·08	7·99
A. M. Peter (Kentucky Experiment Station)	14·02	8·03
H. E. Curtis (Kentucky Experiment Station)..	13·99	7·93
Average of whole number.. ..	13·91	7·80
,, twenty	13·96	7·81

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

Kjeldahl Method.

Analysts.	Per cent nitrogen. No. 3.
Walker Bowman (Virginia Experiment Station)	13·35
R. C. Kedzie (Michigan Agricultural College Experiment Station)	13·72
H. R. Baldwin (West Virginia Experiment Station)	13·45
F. B. Carpenter (North Carolina Experiment Station)	13·40
H. J. Patterson (Maryland Experiment Station)	13·55
B. F. Finney (Virginia Experiment Station)	13·72
R. H. Gaines (Virginia Department of Agriculture)	13·77
T. C. Trescot (United States Department of Agriculture)	13·16
J. M. Bartlett (Maine Experiment Station)	13·54
L. H. Merrill (Maine Experiment Station)	13·63
W. H. Beal (Massachusetts Experiment Station)	13·26
F. W. Morse (New Hampshire Experiment Station)	13·31
C. L. Parsons (New Hampshire Experiment Station)	13·46
C. D. Woods (Stoors Experiment Station)	13·49
Duncan Adriance (Texas Experiment Station)	13·07
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	13·43
L. A. Voorhees and C. S. Cathcart (New Jersey Experiment Station)	13·46
B. B. Ross (Louisiana Experiment Station)	13·71
G. L. Holter (Pennsylvania Experiment Station)	13·08
M. A. Scovell (Kentucky Experiment Station)	13·63
A. M. Peter (Kentucky Experiment Station)	13·53
H. E. Curtis (Kentucky Experiment Station)	13·49
Average	13·46

Ruffle Method.

Analysts.	Per cent nitrogen. No. 1.	No. 2.	No. 3.
F. B. Carpenter (North Carolina Experiment Station)	13·49	7·41	13·39
H. J. Patterson (Maryland Experiment Station)	13·72	7·70	13·71
T. C. Trescot (United States Department of Agriculture)	13·82	7·75	13·55
W. H. Beal (Massachusetts Experiment Station)	13·84	7·62	13·28
G. L. Holter (Pennsylvania Experiment Station)	13·30	7·80	—
Average	13·63	7·66	13·48

Soda-Lime Method.

Analysts.	Per cent nitrogen. No. 3.
H. J. Patterson (Maryland Experiment Station)	13·73
H. E. L. Horton (United States Department of Agriculture	13·46
W. H. Beal (Massachusetts Experiment Station)	13·29
C. D. Woods (Stoors Experiment Station)	13·56
New Jersey Experiment Station	13·44
G. L. Holter (Pennsylvania Experiment Station)	13·30
Average	13·46

Absolute Method.

Analysts.	Per cent nitrogen. No. 1.	No. 2.
T. C. Trescot (United States Department of Agriculture)	13·77	7·79
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	—	7·67

Table of Averages.

Method.	No. of sample.	No. of analysts.	Per cent nitrogen. Average.	Highest.	Lowest.	Diff.
Kjeldahl	3	22	13·46	13·77	13·07	0·70
„ modified for nitrates	1	22	13·91	14·20	13·40	0·80
	2	21	7·81	8·40	7·36	1·04
Ruffle	1	5	13·63	13·84	13·30	0·54
	2	5	7·66	7·80	7·41	0·39
	3	4	13·48	13·71	13·28	0·43
Soda-lime	3	6	13·46	13·73	13·29	0·44

All of the chemists represented reported results by the official methods; those reported by the alternate are in addition to the official.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 30TH, 1892.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, February 6th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, 179 were found to be clear, bright, and efficiently filtered, three being recorded as "very slightly turbid" (V.S.T.).

Except for the occurrence of these three instances of but "very slight turbidity," the condition of the water supply to the metropolis during the month of January was entirely satisfactory. Thus, taking the Thames-derived supply for comparison, the mean degree of colour-intt was found to be 12·4 : 20, as against 18·7 : 20; the mean amount of oxygen expended in oxidation to be 0·052 grain, as against 0·079 grain; and the mean amount of organic carbon to be 0·158 part in 100,000 parts, as against 0·240 part in the previous month's supply. Moreover, the maximum amount of organic carbon in any single sample examined was found to be reduced from 0·319 part in December to 0·204 part in January, the next highest amount recorded during the month being only 0·189 part in 100,000 parts of the water.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE USE OF ASBESTOS IN FILTRATION.

By W. P. BARBA.

In the usual manner of determining manganese by Ford's admirable method, a great deal of time is used up in avoiding the difficulties introduced by the silica present in the steel or iron. The solution of the drillings in HCl, the expulsion of the HCl by HNO_3, and the tedious filtration on the pump, may all be avoided by the use of finely divided asbestos in HNO_3, as pointed out by me in the filtration of carbon sponge (*Journal of Analytical and Applied Chemistry*, vol. v., 596).

The asbestos is best prepared by triturating in a porcelain mortar to moderate fineness, washing with HNO_3, and may be kept suspended in strong HNO_3 for use. The method as now practised at Midvale may readily be carried through in forty minutes, and is as follows:—

5 grms. of steel are dissolved in 80 c.c. HNO_3, specific gravity 1·20, and boiled to one-half that bulk. 75 c.c. of strong HNO_3 are then added, and boiled for about five minutes more. The usual portion of $KClO_3$ is added—about 5 grms.—and the solution boiled till precipitation is effected. The beaker is then withdrawn from the plate and a quantity of finely divided asbestos in HNO_3 is added. The solution, when sufficiently cooled, is filtered on a tight asbestos plug, washed twice with HNO_3, and then with water till all acid is removed. The plug with the precipitate is blown back into the same beaker, ferrous sulphate added, and the titration carried out as usual.

It will be found that filtration is very much facilitated by the presence of the fine asbestos, and that the solution of the precipitate in the $FeSO_4$ is almost instantaneous, thus removing the difficulties of the two most tedious operations of the method.—*Journal of Analytical and Applied Chemistry*, vi., No. 1.

ON THE MOST HIGHLY OXIDISED COMPOUND OF SULPHUR.

By MORITZ TRAUBE.

Berthelot (*Comptes Rendus*, cxii., p. 1481) and Hugh Marshal (*Proc. Chem. Soc.*, 1891, p. 771) have demonstrated the true existence of a persulphuric acid, $H_2S_2O_8$. Both these chemists considered themselves thereby entitled in denying the existence of the compound SO_4 (*Berichte*, xxix., 1764) which I had demonstrated, though without any re-examination of my experiments. In consequence, I considered a repetition of my experiments necessary, which has been kindly undertaken by W. Traube. The former results have been completely confirmed.

The solution of the substance in question in phosphoric acid was obtained as before, by treating the electrolytic 70 per cent sulphuric acid with excess of barium phosphate. Its active oxygen, *i.e.*, that which oxidises ferrous sulphate, was titrated with a solution of this salt. The precipitate of barium sulphate, obtained by boiling the phosphoric solution with hydrochloric acid and barium chloride, was extracted in some cases with dilute boiling hydrochloric acid in order to remove any barium phosphate which had been carried down; in other cases it was first treated in the cold with a dilute solution of soda, and then afterwards with hydrochloric acid.

Hydrogen peroxide was not present if the electrolysed acid was used for analysis whilst recent, or, if it was formed in small quantities, after standing for several days it was destroyed as previously, *before* the determination of the active oxygen by the quantity of permanganate required.

The analysis of three different phosphoric solutions gave the respective mean quantities of 15·0 m.grms., 18·1 m.grms., and 15·7 m.grms. of active oxygen. The proportion of O to SO_3 was 1 : 5·1. Six parts by weight of the sulphur compound, 5 parts by weight SO_3, 1 part by weight of oxygen being eliminated.

Hence, there doubtless exists in the electrolysed sulphuric acid not persulphuric acid but SO_4; for we cannot assume that so indifferent a substance as barium phosphate can split up persulphuric acid into SO_4 and H_2SO_4. On the other hand, it is quite intelligible that on saturating the electrolysed sulphuric acid with strong bases, SO_4 and H_2SO_4 may combine under their influence to persulphuric acid.

In my former investigation I was led by my experiments on electrolysed sulphuric acid saturated with strong bases to the conclusion that SO_4 is indifferent. I had, of course, taken as my point of departure the assumption (seemingly a matter of course), that the solution, when neutralised, contains SO_4. But, as already mentioned, on saturating electrolysed sulphuric acid with an alkali, there is formed a persulphate. The question of the indifference of SO_4 must therefore be decided by further researches. Preliminary experiments with the phosphoric solution of the compound in question seem to confirm its indifferent character.

On the basis of experiments I have placed SO_4—which must now be considered as persulphuric acid—along with the holoxides, the compounds of the type of hydrogen peroxide, because in the first place it very readily forms hydrogen peroxide; secondly, like this, it evolves oxygen with the peroxides of lead, manganese, and silver, in presence of acids, and, thirdly, that it is decomposed in contact with platinum and acids, with liberation of oxygen.

On the contrary, Berthelot and Marshal ascribe to persulphuric acid the same constitution as to permanganic and perchloric, although the latter do not evince the characteristic reactions of the holoxides, and permanganic acid even destroys hydrogen peroxide energetically. Marshal himself has observed that potassium persulphate is not isomorphous with potassium perchlorate.—*Ber. Deutsch. Chem. Gesell.*

THE DIRECT COMBINATION OF CHLORINE WITH METALS.

By U. KREUSLER.

A memoir by Gautier and Chaubry (*Comptes Rendus*, vol. cxiii., pp. 597—600), on "The Direct Combination of Chlorine with Metals," recalled to the mind of the author an observation made some time ago. Among the instances given in the text-books for demonstrating combustion in chlorine gas, there figures a spiral of thin brass wire, to which was attached a tuft of spurious leaf-gold to facilitate ignition.

The text generally speaks simply of chlorine, but sometimes of dry chlorine gas. The drying process is mostly dispensed with, and the experiment, as it is well known, succeeds very easily. But when the author once by accident used the dried gas, it failed unexpectedly, and the metallic surfaces remained perfectly bright. The remembrance of certain kindred phenomena, recently observed in case of oxygen, showed an escape from the difficulty. It was sufficient to allow a drop of water to fall anywhere into the vessel or to insert a moistened glass rod in order to induce immediate and energetic combustion.

It may be mentioned that the gas in question had not been dried with especial care. It had been simply passed through a washing-bottle filled with sulphuric acid and collected by displacement in dry bottles. Powdered antimony caught fire at once in the gas, either because the co-operation of water is not needed in this case, or because sufficient moisture adhered to the material.—*Ber. Deut. Chem. Gesell.*, vol. xxiv., p. 3947.

ON THE

STABILITY OF SILVER SULPHITE.

By W. H. SODEAU.

ACCORDING to Berthier (*Ann. Chem. et Phys.*, vol. iii., 7, 82), silver sulphite is decomposed when boiled with water or heated to 100° C. in air. The blackening of the silver precipitate on boiling is sometimes given as a confirmatory test for sulphites. According to Muspratt, silver sulphite becomes dark purple and ultimately black on exposure to air, but according to Fourcroy the crystals are unaltered even in sunlight. (Quoted in Watts's "Dictionary," old edition).

To prepare the substance used in this investigation, re-crystallised $AgNO_3$ was dissolved in water, and SO_2 passed into the solution; the precipitate (consisting of anhydrous needles, $\frac{1}{250}$th inch and less in length) was well washed by decantation with warm distilled water, and dried in a vacuum over H_2SO_4, saturated with chromic acid, taking special precautions to avoid reductions by the volatile compounds in the vaseline used to render the apparatus air-tight. Several specimens were thus prepared and divided into small portions, which were introduced into tubes, some dry, and others with water, and sealed. The tubes were then heated or exposed to light, with the results given in the table. The mixtures mentioned are intended to roughly indicate the amount of darkening, but are not intended to represent the actual colour.

Condition.	Treatment.	Result (parts by weight).
Dry.	100° C. for 1 hour	Slightly affected, whiter than ordinary white paper.
„	130° C. for 1 hour	About as dark as 1 part graphite, 8 parts $CaCO_3$.
„	200° C. for ½ hour	About as dark as 1 part graphite, 2 parts $CaCO_3$.
„	Placed substance on porcelain at about 400° C.	Became black in a few seconds.
In water.	100° C. for 1 hour	About as dark as 1 part graphite, 25 parts $CaCO_3$.
Dry.	Daylight at south window for two weeks.	About as dark as 1 part graphite, 50 parts $CaCO_3$.
In water.	„ „	About as dark as 1 part graphite, 30 parts $CaCO_3$.

Some silver sulphite which had been exposed to dry air for four weeks was found to contain only a minute trace of sulphate. A portion was kept under water and exposed to air; a small quantity of sulphate was detected after two weeks.

Chemical Laboratory,
King's College, London, W.C.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 12th, 1892.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

THE Report of the Council was read by the PRESIDENT, as was also the obituary notices of Prof. W. Weber, late Honorary Member, Mr. W. G. Gregory, and Prof. James Couch Adams. A list of additions to the Library accompanied the Report.

Dr. E. ATKINSON read the Treasurer's Statement, showing a gain of about £240.

On the motion of the President the Reports of the Council and of the Treasurer were unanimously adopted.

Prof. Van der Waals was elected an Honorary Member of the Society.

Prof. REINOLD proposed a cordial vote of thanks to the Lords of the Committee of Council on Education for the use of the rooms and apparatus in the Royal College of Science. This was seconded by Prof. S. P. THOMPSON and carried unanimously. A similar note was accorded to the auditors, Dr. Fison and Mr. H. M. Elder, on the motion of Mr. W. BAILY, seconded by Dr. C. V. BURTON.

The following gentlemen were declared duly elected to form the New Council:—

President—Prof. G. F. Fitzgerald, M.A., F.R.S.

Vice-Presidents—Prof. A. W. Rücker, M.A., F.R.S., Walter Baily, M.A., Prof. O. J. Lodge, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S.

Secretaries—Prof. J. Perry, D.Sc., F.R.S., 31, Brunswick Square, W.C., and T. H. Blakesley, M.A., M.I.C.E., Royal Naval College, Greenwich.

Treasurer—Dr. E. Atkinson, Portesbery Hill, Camberley, Surrey.

Demonstrator—C. Vernon Boys, F.R.S., Physical Laboratory, South Kensington.

Other Members of the Council—Shelford Bidwell, M.A., LL.B., F.R.S., W. E. Sumpner, D.Sc., Major-General E. R. Festing, R.E., F.R.S., J. Swinburne, Prof. J. V. Jones, M.A., Rev. F. J. Smith, M.A., Prof. W. Stroud, D.Sc., L. Fletcher, M.A., F.R.S., G. M. Whipple, D.Sc., James Wimshurst.

A vote of thanks to the officers of the Society was proposed by Mr. SWINBURNE, seconded by Mr. A. P. TROTTER, and carried unanimously.

The CHAIRMAN then invited suggestions towards improving the working of the Society.

In response, Prof. S. P. THOMPSON said that as the Society has been established fifteen or sixteen years, and had amply justified its existence, the time had now arrived for giving fuller recognition to the privileges of members. He thought they had earned the right to be called "Fellows," and that this ought to be signified by some distinctive title.

Mr. J. SWINBURNE suggested that before papers were brought before the meetings they should be read by a Member of the Council. If suitable, they should then be printed and proofs sent to members who applied for them. Mathematical papers could then be taken as read; and the discussions would be more interesting and to the point. It would also be an advantage if communications on kindred subjects could be taken the same day and discussed together. Papers on purely technical subjects should go to the Technical Societies.

Prof. AYRTON, in reply to Mr. Swinburne, said the members had the matter of papers in their own hand, for, as pointed out in the Report of the Council, if they would only send in the papers early enough, the secretaries would be glad to group them in the way suggested.

Referring to Prof. THOMPSON'S remarks, he said he had often thought it would be an advantage to have another class of members in the shape of "students," who should hold meetings amongst themselves.

Mr. A. P. TROTTER said the Society was unique in many respects, and thought it was not desirable to have different grades of membership.

Dr. C. V. BURTON agreed with Mr. Trotter, and said that, even if Prof. Thompson's suggestion was adopted, means should be provided that persons could be admitted into the Society without claiming any distinction therefrom.

Prof. S. P. THOMPSON, referring to the communications brought before the Society, said it was not necessary that all should possess great novelty. Descriptions of new arrangements of apparatus, of diagrams, and exhibits of modern instruments were of great interest to members.

The CHAIRMAN pointed out that at the early meetings of the Society exhibitions of instruments were frequent, and said the Council would be glad if instrument makers would send apparatus to be shown at any of the meetings.

The meeting was resolved into an Ordinary (Science) Meeting, and Messrs. W. R. Bower and E. Edsen were elected Members.

Prof. S. P. THOMPSON communicated a "*Note on Supplementary Colours*," and showed experiments on the subject.

As white light can be divided into pairs of "complementary colours," so any coloured light, not monochromatic, can be split up into pairs of tints; these the author, for want of a better name, has called "supplementary colours." For producing such colours, two methods were used.

In the first one, a spectrum of coloured light was formed by a direct-vision spectroscope and re-combined on a screen. By interposing a narrow prism between the spectroscope and screen, a portion of the spectrum was separated from the rest, and various pairs of supplementary colours thereby obtained.

In the other method, polarised light, a quartz plate, and a double-image prism were used to form two patches of complementary colours. On interposing a coloured medium, the patches became supplementary and varied in tint as the prism was rotated. The chief peculiarity of supplementary colours was the great variety of tints that could be obtained from a single medium; permanganate of potash in dilute solutions being particularly rich in this respect. The author had also noticed that the eye was not very sensitive to orange coloured rays. When experimenting by the second method he had observed that with any composite light one of the supplementary patches could be got of a greyish hue, and the other nearly a pure spectrum tint. He thus unexpectedly verified Abney's law that any colour could be produced by diluting some spectrum tint with white light.

Capt. ABNEY said that it was very interesting to see the grey colour and the supplementary colours shown by the author. Genl. Festing and himself had experimented on colour phenomena by methods quite different from those used by Prof. Thompson, for they had matched colours by adding white light to pure spectrum tints until a match was produced. Greater purity of colour could be obtained in this way.

A paper "*On Modes of Representing Electromotive Forces and Currents in Diagrams*," by Prof. S. P. THOMPSON, F.R.S., was postponed.

NOTICES OF BOOKS.

Cooley's Cyclopædia of Practical Receipts and Collateral Information in the Arts, Manufactures, Professions, and Trades; including Medicine, Pharmacy, Hygiene, and Domestic Economy. Designed as a comprehensive Supplement to the "Pharmacopœia, and General Book of Reference" for the Manufacturer, Tradesman, Amateur, and Heads of Families. Seventh Edition. Revised and greatly Enlarged by W. NORTH, M.A., F.C.S. London: J. and A. Churchill. Large 8vo., 2 vols., pp. 1827.

THIS valuable and generally admired work is now much more than a mere collection of recipes, however complete. Subjects not merely medical, pharmaceutical, or chemical, are made the subject of able articles in its pages.

Thus, in turning the volumes over, we find notices of anachronism, anagram, anastatic printing, arabesques, arcuduct, aurora, bells, and telephones. In short, the work has a general encyclopedic character, and we are sometimes perplexed to see why the lines have been drawn precisely as we find them. If, *e.g.*, bells are to be included why not cymbals and drums? If telephones are noticed why not telegraphs? We must not be understood as denying the fact that a great part of the book is devoted to such classes of subjects as balsams, plasters, pills, powders, oils, ointments, solutions, &c. Secret medicines and modes of treatment are also dealt with more in the interest of the public than of the advertising fraternity. But we see no mention of electropathy, the ammoniophone, the faith-cure, or not a few of the other fashions of the day.

There are a number of able articles on different subjects connected with sanitary science, though the dissertation on sewage treatment might be, in our opinion, improved by a judicious revision. But the statements of the Rivers' Pollution Commission are still reproduced without the grain of salt. We find a statement by an author whom we shall not advertise, to the effect that: "There is no chemical process that cannot be worked to greater advantage during two months of the year than during twelve, or applied to a small quantity of sewage at a less cost than to a large." It is difficut to imagine by what process this paradoxical conclusion can have been reached. It is a general rule that so long as a raw material can be always obtained, it is more profitable to work all the year round than for a short time, and also on a large than on a small scale. All industrialists are aware of the impolicy of allowing plant and machinery to stand idle.

The series of articles on the diseases of crops occasioned by insects, parasitic microphytes, &c., are excellent,—those, at least, which bear the signature of Mr. Whitehead. Some unsigned passages on similar subjects are drawn up on ultra-Watertonian principles, and would seem by implication to discountenance the destruction of locusts, &c.

We find a few legal articles bearing on sanitary questions, such as common lodging-houses, notification, nuisances, infectious diseases, &c., and which will be serviceable as calling the attention of householders to their responsibilities.

The adulteration of food and drugs has also not been ignored, though the author wisely does not attempt to instruct the lay reader in the detection of this class of frauds.

The articles on dyes and colours are, perhaps, the least satisfactory part of the work, such important classes of tinctorial agents as the azo-dyes having been omitted.

We cannot do otherwise than pronounce the work on the whole most satisfactory. If we may venture on a suggestion we should recommend that in the certain case of a new edition the writers should take their point of view not from the United Kingdom, but from the British Empire. This extended aim would, of course, necessitate the revision of the sections on sanitary topics, on diseases, and on the pests affecting crops.

Systematic Mineralogy, based on a Natural Classification. With a General Introduction. By THOMAS STERRY HUNT, M.D., LL.D. New York: Scientific Publishing Co.

OF all the sciences which treat of visible, tangible objects and their mutual relations, mineralogy is, at any rate in Britain, the least popular. It is also the one which has been least fecundated by the grand principle of evolution. Whether these two facts, both, in our opinion, worthy of regret, are causally connected, we do not venture to decide. We may, however, venture to hope that the appearance of Dr. Hunt's elaborate work will attract more public attention to a science which combines in no small degree intrinsic interest and practical importance. It will be known to our readers that among systematic authors on mineralogy there have appeared two conflicting systems. We have the natural-history method, —a cumbrous word,—and the chemical method, the

former advocated by Mohs, Dana, and Breithaupt, and the latter supported by Berzelius and Rammelsberg.

Our author aims at a reconciliation of these two seemingly conflicting principles. He argues, with full justice, that "chemical and physical characters are really dependent on each other, and present two aspects of the same problem which can never be solved but by the consideration of both."

In his first chapter Dr. Hunt ventures on a step of doubtful expedience, a re-classification of the sciences, which he arranges as physiography and physiology. He is perfectly correct in stating that "the words physiologist and naturalist were formerly synonymous in the English language." But the term physiology has by common consent been restricted to the functional activity of plants and animals, and any return to the old usage will merely promote confusion. He places morphology under the head of bio-physiology, whilst its true position is surely along with taxonomy (botany and zoology), under the descriptive or, better, the statical phase of organic science.

We must here remark that on the Continent biology is made nearly synonymous with physiology, whilst with us it is the sum total of organic science, and divided into a statical phase (morphology and taxonomy), and a dynamical phase (embryology and physiology).

The author in setting forth the chemical basis of his system, proposes four classes, metallaceæ, halidaceæ, oxydaceæ, and pyricaustaceæ. The first of these classes embraces the metals, their alloys and their compounds with sulphur, selenium, tellurium, phosphorus, arsenic, antimony, and bismuth. This first, or metallic class, is sub-divided into two groups, metallometallata and spathometallata.

The halidaceæ consist of four orders, the fluorinea, the chlorinea, the brominea, and the iodinea. The oxydaceæ include the oxides, borates, carbonates, aluminates, silicates, alumino-silicates, phosphates, arsenates, sulphates, &c. Dr. Hunt's last class, the pyricaustaceæ, is divided into carbata, forms of carbon, and hydrocarbata, petroleum, resins, asphalts, and coals. For the details of this system we must refer our readers to the work itself, remarking that the principles of descriptive and determinative mineralogy are not here brought forward.

We cannot discover the author's position with regard to the principle of evolution. He, however, pronounces Mr. Ridsdale's hypothesis of the "survival of the most inert," to be "but another statement of the formula of the survival of the fittest." Precisely so, but it is a statement applicable to the conditions of objects which have no vital cycle and no successions of generations, seeing that nothing further has been heard of Brame's "utricular condition." The student of mineral chemistry cannot, we think, be indifferent to Dr. Hunt's work.

Scientific Correspondence of Joseph Priestley. Ninety-seven Letters addressed to Joseph Wedgwood, Sir Jos. Banks, Captain James Keir, Jas. Watt, Dr. W. Withering, Dr. Benjamin Rush, and others. Together with an Appendix:—I. The Likenesses of Priestley, in Oil, Ink, Marble, and Metal. II. The Lunar Society of Birmingham. III. Inventory of Priestley's Laboratory in 1791. Edited, with copious Biographical, Bibliographical, and Explanatory Notes, by HENRY CARRINGTON BOLTON. New York: Privately Printed.

DR. CARRINGTON BOLTON has already made a very valuable contribution to the early history of chemistry in the shape of a work showing the light which alchemy receives from a study of numismatics. He now confers an additional benefit upon the chemical world by a work which brings into fuller relief the opinions and character of one of the most remarkable—and, we might say, epoch-making—men of the last century. Every chemist knows that, in addition to his important researches on gases, Priestley was the "first and true" discoverer of oxygen, and that he still adhered to the phlogiston system which he had thus undermined. But from this volume we learn for the first time that to the end of his days phlogiston was his "dominant idea," and that he continued to hope for the refutation of the Lavoisierian system and of the restoration of phlogiston to its old prominence.

Another of the unfortunate phases of his character is also noticed. It is well known that his attention was not solely confined to chemistry, or, indeed, to science in general. Much of his time was frittered away on theological and political discussion. His friend Edward Gibbon had recommended him to keep to science and leave miracles alone, reminding him that if Servetus is now remembered, it is not on account of his denial of the doctrine of the Trinity, but because he was one of the forerunners of William Harvey. This good advice, however, was thrown away. We read here that: "Believing as he did that his reputation would be founded on his theological system, Priestley, in his Memoirs, has but little to say of his work in science; and Mr. Rutt, evidently sharing this view, adds nothing whatever which can extend or illustrate Priestley's reputation as a chemical philosopher." *Hinc illæ lachrymæ!* Priestley was not a martyr of science; he was persecuted not as a *savant*, but as a religious and political heretic, whose chemical discoveries, in those critical times, were not considered sufficient to outweigh his other shortcomings.

It can scarcely be denied that by taking the part he did, he to some extent brought science into contempt alike with the ruling powers and with the mob. It appears that during the Birmingham riots the cry was raised "No philosophers," and that some persons to escape the fury of the rioters wrote "No Philosophers" on the front of their houses. The "Lunar Society"—an unhappily named scientific society, at Birmingham—seems never to have recovered from the shock of the riots. The old members died, and no successors were elected in their room. We have never been able to suppress our regret that Preistley had not given his undivided attention to chemistry, and the perusal of these letters by no means alters our view. If in such a fraction of his time he effected so much, he would surely have done more could he have kept out of the bitter waters of controversy. It may, however, still be contended that the versatility and restless activity of his disposition would not have allowed him to devote his life to one subject.

We find here an acknowledgment on the part of Priestley that he was more happy in observing phenomena than in their interpretation; a statement which his career fully bears out. As an observer he was wonderful.

We note (p. 206) an utterance against which we must protest. Says Dr. Carrington Bolton: "The French theory of combustion was but slowly accepted by the conservative Englishman." In our day, France is the country in which new scientific theories meet with the tardiest acceptance!

Dr. Carrington Bolton's work reminds us strongly of the parallelism between Priestley and Lavoisier; both great chemists, rivals for *the* capital discovery of their time, and persistent opponents in theory; both involved in the tempest which enwrapt the close of the eighteenth century; the one done to death by the Revolution to the cry "the Republic has no need of chemists;" the other hunted about by the opponents of the revolution to the equally brutish cry "No Philosophers."

We have here a subject for a modern Plutarch. Should such an one spring up, he will find the collection of letters before us a valuable material for his task.

Dr. Bolton's work can only be obtained from Mr. Edmund F. Brown, 180, Warren Street, Brooklyn, N.Y., the price being $2½ per copy.

Researches on Sodium Isopropylate.—M. de Forcrand.—Sodium isopropylate is a perfectly white powder, which can be preserved only in bottles hermetically sealed and filled wth hydrogen or nitrogen. Its composition is $C_6H_7NaO_2$.—*Comptes Rendus*, cxiv., No. 6.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I should like to be allowed space for a short reply to the letters in your last issue commenting on mine on p. 84.

Mr. Allen's is open and honest, but, fortunately or unfortunately, he is gifted with a vivid imagination, and consequently many of the assertions contained in his letter would in any one else be characterised as reckless: they have no tangible basis. One or two by way of sample.

No. 1.—In reference to the omission of the words "consulting and"—which, by the way, Mr. Allen quotes "and consulting"—he accuses me of suggesting "that the omission was designed." What I really did say was "ill-natured people might be inclined to think" that the omission "was not entirely undesigned on the part of the authors of the circular." Here we have the minor and major premises of a syllogism (in Barbara), and if these are both true the Conclusion must be "Mr. Groves is an ill-natured person." I am sure Mr. Allen would be the first to protest that he had not this in his mind when he wrote his letter. A piece of advice: "Verify your references."

No. 2.—In another part of his letter he says:—"*I myself, with scores of others, heard Mr. Groves . . .*" Here the vivid imagination comes into play. Mr. Allen pictures himself rising with dignity in the presence of a large and attentive audience to ask the Secretary a question. "Scores of others!" Scores demands two scores at least, it *implies* a good many scores. Let us look for a moment at the facts. At Dr. Odling's address on the Tuesday there was a good audience, but the next day the attendance was thin, I had almost said meagre; at all events, it was so when I was there. At one time there were 38 people in the room besides the President and Reporter—that makes 40; there might possibly have been one or even two more—that would make 42, and would entitle Mr. Allen to his "scores of others." It is a nicely rounded phrase.

No. 3.—"*I myself, with scores of others, heard Mr. Groves state* that the papers and discussions at the May Conference would be published in full."

Mr. Allen can of course speak for himself as to what he heard, but is he authorised by the "scores of others" to say what *they* heard? It is not everyone who is gifted with a vivid imagination. Apparently the unfortunate "shorthand writer" who "attended and took verbatim notes of the discussions" was not. Let us see what this dull, unimaginative person wrote down as the verbatim report of the Secretary's reply to a question put by Mr. Allen (I quote from the shorthand writer's report):—

"The Secretary (Mr. Groves) said that it was not intended to publish the discussion in full."

Your readers will observe that the only difference between Mr. Allen's report of what I said and the shorthand writer's is the word "*not*;" but its omission slightly alters the sense. My own impression is that the reporter's version is correct.

I might criticise every paragraph, every sentence almost in the same way, but I should weary your readers and have to discuss matters which I did not touch on in my first letter; moreover, it would not be fair to Mr. Allen, for I know that he, at all events, has written his letter in all honesty of purpose. If instead of being like David in his haste he had carefully eliminated everything which was doubtful before sending in that letter, I believe I should have been able to cordially agree with nearly all that was left.

As regards Mr. William Thomson. He tells us it is the printer's fault that a garbled quotation from the Charter was given in the circular bearing his signature. It is very unfortunate that the printer should have omitted the *two* words "consulting and," thereby entirely altering the meaning of the quotation. If he had left out one of the two only, the omission would of course have been at once detected by Mr. Thomson when correcting the proof. Except in the list of names, this, however, appears to be free from mistakes, even in the punctuation, although Mr. Thomson apologises as not having had time to revise the proof as carefully as he should have wished. I congratulate him on his skill.

In reference to his assertion that a pledge was given "to publish a *full* report of the proceedings of the Conference of the Institute," I can only repeat what I have already said, "This statement is—to speak quite plainly—untrue."

Again, Mr. Thomson, fired with virtuous indignation, writes:—"I am sorry Mr. Groves wrote the last paragraph of his letter, because it insinuates sinister motives on the part of gentlemen who, no one could doubt, would fully uphold the integrity and dignity of the Institute."

The paragraph referred to asks the members of the Institute to frustrate the attempt to hand over the Institute to the public analysts (*i.e.*, "members of the Society of Public Analysts").

Your readers will scarcely credit it, but the printing ink on the Chemical News of Feb. 19, in which that paragraph of Mr. Thomson's appeared, was hardly dry when he indited a circular. That circular directs that seventeen names should be struck out of the voting list as sent out by the Council,—in fact, with the exception of five, to eliminate every one of the ordinary members of Council who are not members of the Society of Public Analysts. The new members proposed are all members of the Society of Public Analysts, with two exceptions.

I state the bare facts, and commend them to the consideration of your readers, together with Mr. William Thomson's letter.—I am, &c.,

Charles E. Groves.

Guy's Hospital, Feb. 23, 1892.

P.S., Feb. 24.—Since writing the above Mr. Allen has kindly sent me a copy of his letter (see below). It gives me the greatest pleasure to find that my estimate of his open, honest character is a just one.—C. E. G.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—Mr. Charles E. Groves informs me that he finds on reference to the verbatim report of the proceedings at the May Conference that, in answer to a question put in open meeting whether it was intended to publish a full report of the proceedings, he replied that "it was *not* intended to publish the discussion in full." I can only express my regret that I and many others misunderstood Mr. Groves's reply, and of course at once accept his disclaimer.

I fail, however, to see that the alteration much improves the position, for it is difficult to understand what justification there could be for spending upwards of £50 in taking verbatim notes of and printing the discussions if it was intended to publish merely an abstract, while even this intention has been abandoned. It appears to me that members of the Institute not able to be personally present at a conference have a right to a full knowledge of the proceedings, especially as a considerable sum of their money was spent in reporting and printing these.—I am, &c.,

Alfred H. Allen.

Sheffield, Feb. 23, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I think a good deal of confusion has arisen in the Institute discussion from a forgetfulness of its early

history. Many of the expressions in the Charter are legacies from the parent society, and should be read by the light of the incidents that gave rise to them.

An outcome of the "black-balling contest" of 1877, the Institute was formed to look after the interests of "chemistry as a profession," in the same way as the Chemical Society is concerned with it as a science. It was called deliberately and comprehensively "The Institute of Chemistry" (and not "The Institute for Analysts").

When the Institute was in embryo we heard only of "committee of chemists," "chemists' organisation committee," "professional chemists," and so forth; *but the Pharmaceutical Society formally objected to this*, and claimed a legal monopoly in the word "chemist" undefined, and a right to prosecute any person not a member of their body who so used it.

Robbed of our birthright by the Pharmacy Act a paraphrase had to be found, and "analytical and consulting chemist" was adopted. This term marked us off sharply from the "chemists" of the Pharmacy Act, and was quite broad enough to cover most professional chemists who cared to join, whether the analytical chemists in works, the analyst pure and simple, or the professor who was open to consultation.

In those days the great idea was to elect on the Council a few representatives of every possible section of applied chemistry, to bind all branches together, and to construct out of these elements a chemical profession that the public could understand.

That was the "elevation" I looked for when, as one of the earliest A.I.C.'s, I joined the Institute—a brigading together for mutual protection of all bonâ fide chemists.

It was also agreed that, however good the training in a private laboratory might be, it was rarely broad enough, and some collegiate education was essential.

I regret very much to find that a section of the society should now be endeavouring to pare down this scheme by a narrow interpretation of phrases forced on us by obstructionists outside our profession.—I am, &c.,

F. Woodland Toms.

Jersey, Feb. 22, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—The victim of misplaced confidence is always interesting. What rogues those printers are, to be sure! and yet how strangely their carelessness and Mr. Thomson's want of time to correct it fit in and aid the Fifty-nine in their attempt to place the Analyst before all.

Thus does chance guide untoward events, printers' errors included.

Of course it was the ink, or the pen, or the paper, or something, which caused the following to appear on p. 2 of the Manifesto:—

"We propose . . . to substitute the names of *Analytical Chemists* in actual practice for those of some of the members nominated on the official list issued by the Council." Or could it have been that careless printer again?

The Council was aware that the refusal to print the discussion of the May Conference would be used against it, but gentlemen able to decide what Council business may or not be treated as an open secret are at least aware that the very best party move that those opposed to Analyst preponderance could have made was to print those speeches as spoken and unedited by the speakers. The majority of the Council, however, considered the reputation of the Institute of more value than a party triumph.

The best antidote to all this exaggerated talk lies in a careful consideration of the *Proceedings*, Part III., 1891, and the "Report of the Council" just issued.

Members who carefully read them and consider the work done will no doubt so use their ballot papers as not to "disagreeably surprise" the "late" (?) Secretary, but the spokesmen of the Fifty-nine.—I am, &c.,

R. J. Friswell.

115, Darenth Road, N., Feb. 22, 1892.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

Sir,—The publication of the letter of your correspondent W. S. on the above subject appears to invite an expression of opinion as to how a Society of Students can best set to work to advance themselves in the Science individually and collectively. There is surely only one answer to your correspondent's questions. Seek first the Science and its discipline and all those *things* shall be added! A College Society devoted to Science, as the universal and particular milch cow, will only help to swell to the flood of mediocrity, which is threatening to put out the fires of genius for ever!—I am, &c.,

C. O. O.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 6, February 8, 1892.

Silica in Plants.—MM. Berthelot and G. André.—The part played by silica in plants, especially in the Gramineæ, raises interesting questions both physiological and practical. Silica takes part in forming the solid framework of plants, and we may ask if it does not take a certain share in the distribution of the nutrient matters. The authors have determined the absolute and the relative proportions of silica in the grain and in the soil. They have made similar determinations in the plant at successive stages of its growth, from germination to fructification, examining successively each of the essential parts of the plant. They operated upon spring-wheat, determining the silica in four forms: total silica, silica soluble in pure water, silica soluble in cold dilute potassa, and soluble in hot dilute potassa. They have reserved the question whether the silica is absorbed as such (pure) or in combination with carbonic or mineral principles. The soil was a sandy loam in which the silica was entirely present in the state of quartz and of stable silicates. The silica of the grain was almost totally in the state of silica soluble in cold dilute alkalis, its total proportion not reaching 1-100th of the weight of the grain. The total weight of silica is greatest in the root. The relative proportions of silica soluble in water or in dilute potassa are higher in the stem. Here nearly three-fourths of the silica are present in a state insoluble in dilute potassa. Before inflorescence the silica of the stem is almost entirely soluble in alkalis. Leaving out of question the roots, which are more or less contaminated by the soil, the total silica is at its maximum in the leaves. The ear is always the part of the plant least rich in silica.

Determination of the Point of Congelation of Highly Dilute Aqueous Solutions: Application to Cane-Sugar.—M. Raoult.—By means of improvements in the refrigerating mixtures and in the agitators employed, the author has obtained more precise determinations than those detailed in his paper in the *Annales de Chimie et de Physique* (Series 6, vol. ii., p. 93, 1884). For weights of sugar from 0·683 grm. to 39·040 grms. per 100 grms. of water the congelation point falls from 0·042°

to 2·274°. He is able to determine reductions in the freezing-point down to 1·500th of a degree.

New Researches on the Solar Atmosphere.—H. Deslandres.—The author, referring to his former paper (*Comptes Rendus*, August, 1891) on photographic researches on the solar atmosphere, comprising the blue, the violet, and the ultra-violet up to λ380, has now extended his examination of the contiguous part of invisible ultra-violet region as far as λ350. He has rediscovered in several of the solar protuberances of the second half of 1891 the series of ultra-violet hydrogen rays detected for the first time by Prof. Huggins in the white stars. He has obtained as many as eight successive brilliant rays all fine and well defined (Mr. Hale had found five of these rays and Prof. Young four), and he does not doubt that at a station on a high mountain the two remaining rays of the series might be detected. Thus the sun, which is a yellow star, presents in certain parts of its atmosphere the characteristic radiation of the white stars. This result confirms our present ideas on the evolution of the stars. He has also obtained a hydrogen ray a little more refrangible than α (λ388), noticed for the first time by Hales, and recently contested by Prof. Young.

Action of Chlorine upon Ruthenium; Its Sesquichloride and Oxichloride.—A. Joly.—The chlorination of ruthenium is effected very precisely either at 360° or 440° on heating the finely divided metal in a mixture of carbon monoxide and chlorine, the latter always in excess. The metal is rapidly converted into a brown powder and increases considerably in bulk. The sesquichloride, $RuCl_3$, is insoluble in cold water and the acids, mineral and organic. Boiling water destroys it slowly; the liquid becomes acid and takes a light blue colour, but the greater portion remains insoluble as a black powder. It dissolves neither in carbon chloride nor disulphide, nor in chloroform, nor phosphorus trichloride, nor ether. If digested for some hours in a sealed tube with 50 parts of absolute alcohol it dissolves slowly, and unattacked ruthenium remains as residue. The alcoholic solution is intensely coloured; in a shallow layer it is of a purple violet, which does not change if preserved in a sealed tube. If exposed to atmospheric moisture, or if the alcohol used as a solvent is alcohol at 95°, it changes in some days to a blue-violet, and then to a deep indigo. This change is most rapid at 60°. The solution in absolute alcohol, if evaporated in a dry vacuum, leaves a brownish residue with bronze reflections. If the blue liquor is distilled it leaves a black product which, if dried in the stove at 150°, has the composition of an oxichloride, $Ru(OH)Cl_2$). The oxichloride is very soluble in water, with an indigo blue colour. The liquid is neutral. If diluted it becomes turbid at the ordinary temperature, and deposits a black-brown flocculent precipitate of ruthenium sesquihydroxide, $Ru(OH)_3$. If the oxichloride is treated in heat with concentrated hydrochloric acid, there is formed a brown solution which turns yellow on dilution. This solution is a hydrochlorate of ruthenium chloride, which at 200° becomes transformed into the anhydrous chloride. At the ordinary temperature soda throws down from solutions of the hydrochlorate, the chloride and the oxychloride, ruthenium hydroxide. Ammonia combines with the oxichloride, forming a product very soluble in water and of the intense red of the alkaline solutions of phenolphthaleine.

On a Silver Nitrosilicate, and on the Existence of a Nitrosilicic Acid.—G. Rousseau and G. Tite.—This paper will be inserted at some length.

Lead Chlorosulphide and Bromosulphide.—F. Parmentier.—The compound obtained on precipitating a salt of lead by hydrogen sulphide in presence of dilute hydrochloric acid, has the composition PbS,PbCl. It is of a cinnabar red whilst suspended in water, but after subsiding it becomes darker. It is not stable, being decomposed by water, acids, and alkalis. Alkalis at first blacken it, and then the black body is rapidly transformed into a white flocculent mass. The bromosulphide, and probably the iodosulphide, are analogous in properties and in composition.

The Decomposition of Sulphurous Acid by Carbon at Very High Temperatures.—M. Scheurer-Kestner.—Sulphurous acid at very high temperatures is decomposed by carbon, forming free sulphur, carbon monoxide, and carbon dioxide. M. Berthelot has shown that at a lower temperature sulphurous acid is converted into carbon monoxide, oxisulphide, and sulphide. The two latter bodies are not permanent at very high temperatures.

A Nitro-derivative of Antipyrine.—Edm. Jandrier.—Nitrodimethyloxyquinizine forms straw-coloured crystals insoluble in cold water, and sparingly soluble in boiling alcohol. Its best solvent is glacial acetic acid. On treatment with zinc and acetic acid it yields amido-antipyrine.

The Rotatory Power of the Diacetyltartaric Derivatives.—J. A. Le Bel.—A controversial paper in reply to a memoir by M. Colson, in the *Comptes Rendus* of January 25th. The author argues that stereochemistry is independent of the hypothesis of the tetrahedron.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 12.

On Nitrised Silk.—Leo Vignon and P. Sisley.—The yellow colour obtained by the action of ordinary nitric acid upon silk is best produced with a mixture of nitric acid and water of the specific gravity 1·133 heated to 45°. After washing in excess of water the silk retains a characteristic yellow colour, fast to air and light. Pure nitric acid, free from nitrous products, gives no colour on silk under the above conditions, but if a little sodium nitrite is added the yellow colour comes up. The tone obtained with nitrous-nitric acid is darkened by a passage through alkalis. It is palest with ammonia and reddest with baryta. Silk nitrised is enriched in nitrogen, and impoverised in carbon and oxygen.

Constitution of Solutions of Salts of Chromium Sesquioxide Modified by Heat.—A. Recoura.—The author has met with three varieties of solutions of chromium sulphate:—1. The violet solution containing the neutral sulphate, which, on evaporation, gives the crystalline violet sulphate. 2. The non-crystalline solution resulting from the action of heat upon the former, and containing free sulphuric acid and the basic sulphate. 3. A green, non-crystalline solution, obtained by precipitating chromium oxide from the former solution and re-dissolving in sulphuric acid. It contains the basic sulphate.

Contribution to the History of the Salts of Nickel and Cobalt.—A. Terreil.—This paper will be inserted at some length as early as possible.

Colorimetric Determination of Iron by means of the Sulphocyanide and some other Coloured Combinations of this Metal.—J. Riban.—It is proposed to determine small quantities of iron, especially in the blood, by transforming them into sulphocyanide and comparing the solutions thus obtained with type solutions containing a known weight of the same sulphocyanide. The paper requires the accompanying tables.

The Reaction of Iodine with Acid Sodium Sulphite.—W. Spring and E. Bourgeois.—A controversial paper, having reference to a paper by Prof. Otto, of Brunswick.

On Acid Potassium Tartrate as Original Standard Substance for Acidimetry and Alkalimetry.—Prof. Dr. A. Bornträger.—The author recommends potassium bitartrate, because it forms anhydrous crystals, is very slightly hygroscopic, can be dried at a high temperature, and preserved for an unlimited time.—*Zeitschrift fur Analytische Chemie*, xxxi., Part 1.

MISCELLANEOUS.

The University of Dorpat.—Many of our readers will learn with righteous indignation that the Russian Government is preparing for the suppression of the time-honoured University of Dorpat.

Royal Institution.—Professor W. P. Ker will, on Thursday next (March 3), begin a course of three lectures on "The Progress of Romance in the Middle Ages." Mr. F. T. Piggott will deliver his Friday evening discourse on "Japanesque," on March 11th, in place of Professor Oliver Lodge, who will give his lecture on "The Motion of the Ether near the Earth" on April 1st.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Medical, 8.30.
—— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).
TUESDAY, March 1st—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30. (Anniversary).
—— Pathological, 8.30.
WEDNESDAY, 2nd.—Society of Arts, 8. "Spontaneous Ignition of Coal and its Prevention," by Prof. Vivian B. Lewes.
THURSDAY, 3rd.—Royal, 4.30.
Royal Society Club, 6.30.
—— Royal Institution, 3. "The Progress of Romance in the Middle Ages," by Prof. W. P. Ker, M.A.
—— Society of Arts, 8. "Indian Sanitation and the International Congress of Hygiene," by Surgeon-Genl. Sir William James Moore.
—— Chemical, 8. "A Rule for Determining whether a given Benzene Mono-Derivative shall give a Meta Di-derivative or a Mixture of Ortho and Para Di-derivative," by Prof. Crum Brown and Dr. Gibson. "The Relative Orienting Effect of Chlorine and Bromine," by Dr. Armstrong and Mr. Briggs. "Contributions to our Knowledge of the Aconite Alkaloids—Part II. The Alkaloids of True Aconitine napellus," by Prof. Dunstan and Mr. Umney; "Part III. The Properties of Aconine—Conversion of Aconine into Aconitine," by Prof. Dunstan and Dr. Paesmore. "Note on the Luminosity of Coal-Gas Glames," by William Foster, M.A.
FRIDAY, 4th.—Royal Institution, 9. "The Surface-Film of Water and its Relation to the Life of Plants and Animals," by Prof. L. C. Miall, F.L.S.
—— Geologists' Association,
—— Quekett Club, 8.
SATURDAY, 5th.—Royal Institution. 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

ENGLISH TRANSLATION OF MENDELEEF'S CHEMISTRY.

The Principles of Chemistry.

By D. MENDELÉEF,

Professor of Chemistry in the University of St. Petersburg.

TRANSLATED BY

GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg,

AND EDITED BY

A. J. GREENAWAY, F.I.C., Sub-Editor of the Journal of the Chemical Society.

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TUESDAY, MARCH 1, 1892.

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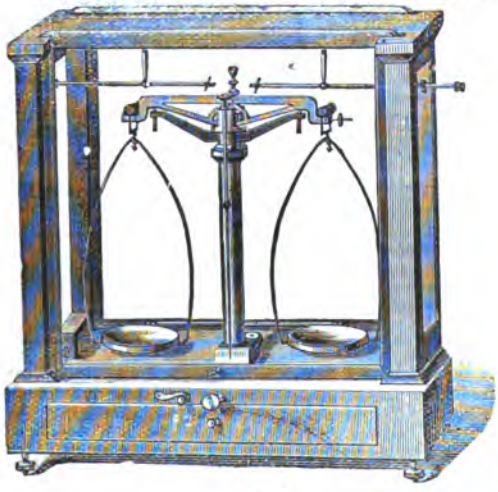

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VOL. LXV., No. 1684.

ON A SILVER NITRO-SILICATE, AND ON THE EXISTENCE OF A NITRO-SILICIC ACID.

By G. ROUSSEAU and G. TITE.

No silver silicate has hitherto been obtained. The experiments of Stas tend to prove that finely divided silver combines with glass heated in a current of air to near its softening point. But the quantity of metal which thus passes into the state of silicate is too slight to warrant the conclusion of the existence of a compound of silver and silica in definite proportions.

The researches about to be described seem to throw some light on this question. They have terminated in the discovery of a complex salt containing silica, nitric acid, and silver oxide.

Although the formation of a basic silver nitrate seemed, from analogy, scarcely probable, we heated in sealed tubes a mixture of 1 mol. of silver nitrate, with from 1—2 mols. of water, in presence of fragments of marble. Up to 180° no insoluble compound was separated out, but the liquid took a pale yellow colour. From 180° and as far as 300° and upwards, we obtained crystals of a ruby-red colour, which adhered strongly to the tubes. They are formed slowly, especially at about 200°. To obtain a practical yield the experiment must be prolonged for sixty hours. The product is always mixed with crystalline tablets of silver carbonate, which are easily separated by levigation.

The composition of the red crystals is—

$$3(2Ag_2O,SiO_2)2AgNO_3,$$

representing a compound of silver silicate and nitrate. But on more careful study it appears that the compound must be regarded as the silver salt of a nitro-silicic acid, $7Ag_2O,3SiO_2N_2O_5$.

The silica is derived from the action of the solution of silver nitrate upon the glass of the tubes. Hence, the crystals obtained in these circumstances are strongly attached to the sides, whence it is often difficult to dislodge them. If we take care to add previously to the mixture of water and silver nitrate a little dry silica, obtained from the decomposition of silicon fluoride by water, we obtain crystals which no longer adhere to the glass.

In order to avoid the formation of silver carbonate we have sought to substitute for the marble either finely-divided silver or silver oxide. In presence of metallic silver the neutral nitrate remained unaffected. Silver oxide gives us better results, on condition of not exceeding the temperature of 200°, but it is always difficult to separate the excess of oxide from the silver nitro-silicate.

We finally succeeded in reproducing this compound by mixing silica, dried at 100°, with dry silver nitrate, kept for some hours in fusion in a crucible of the same metal at temperatures of from 350—440°. The crystals thus obtained in the dry way are much smaller than those formed in sealed tubes in consequence of the greater rapidity of their formation.

Silver nitro-silicate appears in the form of short prisms of a ruby-red colour when seen by transmitted light, if sufficiently thin and presenting longitudinal extinctions in parallel light. When thicker they become opaque, and appear then of a bluish-black by reflected light.

If heated to dull redness these crystals melt, with intumescence, giving off nitrous vapours. The residual white, porous mass resulting from the ignition seems to contain reduced silver and an acid silicate, Ag_2O,SiO_2. The conversion of the original substance into silicate, metal, and nitrous vapours seems to take place according to the equation—

$$7Ag_2O,3SiO_2,N_2O_5 = 3(Ag_2O,SiO_2) + 4Ag_2 + 2NO_2 + O,$$

corresponds in fact to a loss of 9 per cent of the theoretic weight. In two experiments we found 8·86 and 9·08, values which agree with moderate exactness. On the other hand, the residue is attacked by the nitric acid with effervescence, and the escape of nitrous vapours, which indicates the presence of metallic silver in the mixture.

Silver nitro-silicate is easily soluble in dilute nitric acid; the solution, clear at first, becomes turbid if concentrated on the water-bath, in consequence of the formation of a deposit of silica. Hydrochloric acid decomposes it instantly, producing silver chloride. We sought to isolate the nitro-silicic acid liberated in this reaction. In contact with a solution of ammonium hydrochlorate the silver salt is destroyed; the liquid takes a strongly alkaline reaction and exhales a decidedly ammoniacal odour. The liquid if filtered to remove silver chloride, and then concentrated in a vacuum, leaves a residue of gelatinous silica.

Potassium chloride in solution seems to be without action even at the temperature of 100°. If it is moistened with a solution of potassium iodide the nitro-silicate at once takes the yellow tint of silver iodide. If we mix the silver salt and the alkaline iodide in the proportion of 1 equivalent of the former to 7 equivalents of the latter, all the silver is separated as an iodide. The filtrate, if evaporated *in vacuo*, leaves long, colourless needles of potassium nitro-silicate.

In a subsequent communication we shall give the composition and the properties of the alkaline nitro-silicates obtained in this manner.—*Comptes Rendus*, vol. cxiv., p. 291.

NOTE ON THE ESTIMATION OF NITROUS ACID.

By ARTHUR G. GREEN and F. EVERSHED.

WE have recently had our attention called to an article by Prof. Lunge on "The Estimation of Nitrous Acid in Sodium Nitrite" in the November number of the *Zeitschrift fur Angewandte Chemie*. In this paper Prof. Lunge makes a critical comparison of the accuracy of various methods which have been proposed, and comes to the conclusion that his modification of the permanganate process is the most accurate.

That his method gives good results when organic matter or other reducing substances are absent we do not doubt, but a method in which these sources of error need not be taken into account is surely to be preferred. Such a method was published by us in 1886 in the *Journal of the Society of Chemical Industry* (vol. v., p. 633), and has since been in constant use in at least one large technical laboratory with satisfactory results. It depends upon the diazotisation of a normal solution of aniline hydrochloride, using starch and zinc iodide as indicator. Prof. Lunge mentions the diazotisation method, but attributes its publication to Boeckmann, stating that it was improved by Schultz (by substitution of sulphanilic acid for aniline), but both these publications were long subsequent to ours. In his examination of the diazotisation method (Schultz's modification) Prof. Lunge arrived at results which were more than 8 per cent too low, and accordingly dismisses the diazotisation method (whether with sulphanilic acid or with aniline) as being entirely inaccurate, expensive, and troublesome, and he considers it should be abandoned altogether. If Prof. Lunge had followed our directions, instead of employing the modification of Schultz, he would probably have arrived at a different conclusion, for in the above mentioned paper we have clearly shown that if aniline hydrochloride is used and proper precautions are taken the method gives results which are sufficiently con-

cordant amongst themselves and only about 0·4 per cent lower than those obtained by Kinnicut's method, which Prof. Lunge approves.

According to our experience, sulphanilic acid (used by Schultz), owing to the slowness of the reaction, is not nearly so suitable for the estimation of nitrous acid as aniline hydrochloride; even with aniline sulphate the reaction is far slower than with the hydrochloride. It is also important to work with tolerably strong solutions, as the more dilute the solution the slower is the reaction.

The following is the method of procedure we employ:—A normal solution of aniline hydrochloride is prepared by dissolving 93 grms. of pure dry aniline, together with 450 c.c. of hydrochloric acid (about 31 per cent HCl), in 1 litre. Of this solution 25 c.c. is placed in a small stoppered bottle surrounded with ice and water, and is titrated with the nitrite solution (made up about normal) with constant agitation. From time to time a drop is taken out and mixed on a white plate with a drop of zinc iodide and starch solution until a blue colour indicates the presence of an excess of nitrous acid. When a slight excess of nitrous acid still remains after the contents of the bottle have stood for an hour, the end-point is reached. In testing with the starch solution account must only be taken of the blue colour which is produced *at once*, as the drop usually turns blue after standing for some time.

ON THE ACTION OF CERTAIN LIQUIDS ON ALUMINUM.*

By Professor GEORGE LUNGE, Ph.D.

Some months ago a paper was published in a German pharmaceutical journal by Lübbert and Roscher on the behaviour of aluminum toward a number of liquids with which that metal might come into contact when made into canteens, cooking vessels, surgical instruments, &c. The conclusions reached by those two observers would be detrimental to the application of aluminum for any use in which it may come into contact with liquids intended to pass into the human body. Before such a conclusion, momentous as it would be for the extension of the use of aluminum in many directions, can be accepted as valid, it ought to be verified by other observers, especially as neither of the above-named gentlemen is a chemist in the proper sense, one being a medical man and the other a pharmacist fresh from his studies.

The method employed by Lübbert and Roscher is anything but trustworthy. In the first instance they did not make any quantitative estimations, but confined themselves to qualitative observations, which may be very deceptive, as some of the substances employed were probably not free from alumina; secondly, they worked exclusively with aluminum foil, which is well known to be much less resisting to chemical action than compact sheet aluminum.

This induced me to take the matter in hand, in conjunction with my demonstrator, Mr. Ernst Schmid, and I will now give a short account of our results:—

Our experiments were all made with commercial rolled sheet aluminum, 1 m.m. thick, from the Neuhausen works, of the following composition:—0·44 per cent combined silicon, 0·11 per cent crystallised silicon, 0·25 per cent iron; traces of copper; 99·20 per cent aluminum (by difference). The sheet was cut up into strips of such a size that they could be conveniently introduced into the flasks serving for our experiments. Each strip was freed from sharp edges by a file, and was thoroughly cleaned in order to lay bare a real metallic surface and remove the excessively compact surface produced by the rolling process. They were for this purpose treated, first with concentrated solution of caustic soda, then with water, then with dilute sulphuric acid, again with water scrubbed with a brush and distilled water, rinsed with alcohol, and dried in an oven. Three such strips were accurately weighed, hung by means of small holes upon a glass hook in such manner as not to touch one another, and introduced into the flasks containing the liquids to be tested. Each flask held about 400 c.c. of liquid, and was closed by a cork through which passed the stem of the glass hook. After leaving the whole for six days at the ordinary temperature of the room, the strips were taken out, rinsed with distilled water, freed from any adhering alumina by means of a soft brush, rinsed with alcohol, dried, and weighed. The loss of weight was referred to the aggregate surface of the three strips (about 130 square centimetres), and is in the following table reduced to 100 square centimetres. Each liquid was tested at least twice in order to guard against accidental mistake. In a few cases, where the nature of the liquids presented no special difficulties, the alumina was, moreover, determined gravimetrically in the liquid after the experiments with results closely approximating those found by ascertaining the loss of weight of the aluminum. The following table gives the results of our experiments.

Liquids experimented upon.	Loss in weight. A. M.g.	B. M.g.	Average. M g.	Reduced to a surf. of 100 sq. c. M g.
Ordinary claret	4·1	3·3	3·7	2·84
„ hock	4·0	4·5	4·3	3·27
Brandy	1·6	1·2	1·4	1·08
Pure 50% alcohol	0·8	0·8	0·8	0·61
5% solution tartaric acid	1·9	2·4	2·2	1·69
1% „ „ „	3·6	3·1	3·4	2·58
5% acetic acid	4·3	5·7	5·0	3·85
1% „ „	6·2	5·2	5·7	4·38
5% solution of citric acid	2·8	2·8	2·8	2·15
1% „ „ „	2·3	2·6	2·5	1·90
5% lactic acid	6·1	6·3	6·2	4·77
5% butyric acid	1·7	1·7	1·7	1·31
Coffee	0·6	0·7	0·7	0·50
Tea	0	0	0	0
Beer	0	0	0	0
4% boric acid solution ..	2·3	2·3	2·3	1·77
5% carbolic acid	0·1	0·5	0·3	0·23
1% „ „	0·8	0·5	0·7	0·49
½% salicylic acid	7·3	9·2	8·3	6·35

In very few of the cases was any action outwardly visible. In the case of brandy and alcohol, where the quantitative action was extremely slight, the surface of the aluminum showed a few fungus-like excrescences, probably formed by alumina and caused by accidental flaws in the sheet. Lübbert and Roscher found that allohol, ether, and all similar liquids had no action at all on aluminum foils, so that the observation made by us would appear to be due to an accidental cause. Only in the last case, that of a solution of salicylic acid, did the aluminum lose its bright surface and become dull.

From our experiments the following conclusions may be drawn:—The action of coffee, tea (both of which had been poured in hot), and beer is zero, or practically so; that of brandy is also extremely slight; the action of acids and acid liquids (wine, sour milk, fruit-juices, &c.) is more pronounced, but even in this case far too slight to cause any alarm whatever. Taking the worst case found, that of acetic acid, we find a maximum attack of less than 5 m.grms. per 100 square centimetres in six days. Now a canteen holding a litre (or nearly a quart) has an inner surface of about 600 square centimetres and an aluminum weight of about 200 grms. Such a canteen would in the very worst case lose 5 m.grms. in a day, even if it were always full, or 1 grm. in two hundred days, and only in fifty-five years would it be reduced to half its weight. This is certainly too trifling a work to be

* *Engineering and Mining Journal.*

practically considered. Nor is there the slightest danger of any injurious action upon the human body by such traces of aluminum compounds, seeing that our food contains very much more of these. Moreover, aluminum compounds are not poisons in the ordinary sense to be compared to compounds of arsenics, mercury, lead, copper compounds, &c.; they cannot act injuriously unless quantities a hundred times larger than those we have found were regularly entering into the human stomach.

The final conclusion must, therefore, be this: that aluminum may, without any fear, be employed for canteens or any other vessels serving for holding articles of food at least at the ordinary temperature.

REPORT ON DETERMINATION OF NITROGEN.*

By E. B. VOORHEES.

(Concluded from p. 100).

Kjeldahl Modified for Nitrates.

Remarks.—The average of the results reported on sample No. 1 is 13·91; excluding two that report much less nitrogen than the sample is shown to contain, the average is 13·96, or 0·05 of 1 per cent less than the calculated percentage.

On a basis of an average of 13·96 per cent, nine chemists are within one-tenth of 1 per cent, the limit usually allowed for experimental error; thirteen chemists, or 65 per cent of the whole number, are within 0·15 of 1 per cent, the limit often allowed between duplicates; twenty chemists, or the whole number included in the average, are within 0·3 of 1 per cent, the limit of error allowed by commercial chemists for what is termed "factory work."

The average of the results on sample No. 2 is 7·81; if we exclude one which is evidently much too high, and one too low, the average remains the same, and is 0·15 of 1 per cent less than the calculated percentage. Eight chemists are within 0·1 of 1 per cent of either the calculated per cent of 7·96 or the average per cent secured of 7·81. Taking 0·2 of 1 per cent as the limit of error, eleven chemists are within the same on the basis of the calculated per cent, while on the basis of the average secured sixteen are within the limit. Inasmuch as more than half the whole number of results reported on this sample are lower than the average of 7·81, the result above noted would seem to indicate either that the calculated per cent was too high or that on a mixture of this character the results secured by the official method are too low. While sample No. 2 is an unusual mixture and somewhat difficult to manage, I am of the opinion that the trouble is not with the method.

If we simply compare the average of this year with that of last year, the results by the modified Kjeldahl show no apparent improvement, yet the fact that the average this year represents the work of twenty-four experiment station chemists, some of whom are reported to be inexperienced, as against fifteen chemists last year, which number included commercial chemists of high standing, it indicates a slight improvement in the work, and seems to me to fully verify the statement made by Mr. Scovell in his report for 1889, viz., "that the modified Kjeldahl method is an accurate and reliable one for the determination of nitrogen in fertilisers containing nitrates."

Kjeldahl Method.

The average of the determination reported on sample No. 3 is practically identical with the calculated percentage. Ten chemists are within 0·1 of 1 per cent of the average, and the difference between the highest and the lowest is but 0·43 of 1 per cent, a result which is highly satisfactory.

Alternate Methods.

The results on Nos. 1 and 2, by both the "Ruffle" and absolute methods, are lower than by the official, though a fair comparison cannot be made owing to the very few reports by these methods. The soda-lime method gave results practically identical with those secured by Kjeldahl.

In accordance with the recommendations made by the reporter in 1889 the chemists of the Kentucky Station reported results secured on official samples Nos. 1 and 2 by substituting for 2 grms. of zinc dust and 2 grms. of salicylic acid, 2 grms. of zinc sulphide and 1 grm. of salicylic acid.

Results.

Analysts.	Per cent nitrogen.		
	No. 1.	No. 2.	Potassium nitrate, C. P.
M. A. Scovell	14·08	7·99	—
A. M. Peters	—	7·82	13·79
H. E. Curtis	13·99	7·76	—
Theoretical	14·01	7·96	13·83
Average association results	13·96	7·81	—

The above results are the averages of several determinations agreeing closely with each other.

A practical test of this method was also made at the New Jersey Station, where thirty-three samples of commercial fertilisers containing nitrate nitrogen, ranging from 0·1 to 2·62 per cent, were duplicated by the official Kjeldahl for samples containing nitrates and by the suggested modification.

2 grms. salicylic acid and 2 grms. zinc dust.	1 grm. salicylic acid and 2 grms. zinc sulphide.	2 grms. salicylic acid and 2 grms. zinc dust.	1 grm. salicylic acid and 2 grms. zinc sulphide.
3·51	3·63	3·22	3·31
3·51	3·59	1·85	1·83
2·53	2·50	4·12	4·09
4·21	4·24	1·10	1·06
4·36	4·32	1·45	1·39
3·03	2·91	2·91	2·85
3·97	4·03	3·31	3·31
2·69	2·78	1·32	1·24
2·22	2·17	1·25	1·31
3·03	3·00	2·82	2·78
4·55	4·56	3·16	3·04
3·54	3·62	2·80	2·74
4·96	4·94	2·41	2·38
3·03	2·99	4·56	4·56
2·69	2·70	3·42	3·34
4·21	4·26	3·18	3·30
4·06	4·07	3·13	3·08
1·90	1·88		

The results were highly satisfactory. The difference in duplicates ranged from nothing to 0·12 of 1 per cent, with an average difference on the whole number of 0·02 of 1 per cent.

Errors Due to Reagents.

A few chemists reported difficulty in securing uniform results on sample No. 1 when different weights were used and the proper deduction made for error due to reagents. This is an important point and should be carefully noted in the study of methods. Mr. Woods, of the Storrs Station, says that "Kjeldahl modified has in blank determinations always given some nitrogen. Should not be surprised at this if it were not that we always obtained about the correct percentage of nitrogen in nitrates (pure salts) without the use of the correction thus obtained, and the results have always been too low when the correction has been used." His report on this point is of considerable value and is appended in full.

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

Modified Kjeldahl Method.

Mean of four "blanks" gave nitrogen corresponding to 0·4 c.c. of ammonia solution, equal to 0·0012 grm. nitrogen.

With potassium nitrate (theory), 13·84 per cent; mean by Tiemann-Schultze method, 13·75 per cent nitrogen.

	Per cent nitrogen.	
	Without correction.	With correction.
	13·75	
	12·78	
	13·76	
	13·68	
Average ..	13·74	13·27

Nitrogen in Samples.

(Percentages calculated on water content at receipt).

No. 1.

	Per cent nitrogen.		
	Tiemann-Schultze method.	Modified Kjeldahl.	
		Without correction.	With correction.
	14·03	14·05	
	14·08	14·01	
	14·16	14·06	
	14·19		
Average ..	14·09	14·04	13·57

No. 2.

	Modified Kjeldahl method.	
	Without correction. Per cent nitrogen.	With correction. Per cent nitrogen.
	7·92	
	8·02	
	7·96	
	7·98	
	8·00	
Average	7·97	7·85

The work of Mr. Woods verifies the experience of the New Jersey Station, where the error due to reagents had previously been shown to be equivalent to 0·0010 grm. nitrogen, and which had produced widely varying results on pure nitrates when the proper deduction had been made for different weights taken, the results being invariably from 0·2 to 0·5 of 1 per cent low when less than half a grm. of the material was taken. The following determinations on sample No. 1 were made to illustrate this point.

Weight taken.	Without correction.	With correction.
Grm.	Per cent.	Per cent.
0·9	13·93	13·82
0·8	14·05	13·92
0·7	14·12	13·98
0·5	14·06	13·86
0·5	14·04	13·84
0·5	14·11	13·91
0·4	14·04	13·79
Average ..	14·05	13·87

The average of the four determinations on one-half grm. or less without correction is 14·05; with correction it is 13·85, or 0·20 of 1 per cent less; the average of the three without correction on more than one-half grm. taken is 14·03; with correction 13·91, or 0·12 less.

It seemed reasonable to infer from this work that the results secured without the deduction for error were nearer to the truth, and hence they have been used in the report rather than the others. Further blank determinations were made with proper precautions at our station, and it was shown that our assumed error was too great, since the variations in the results ranged from an equivalent of 0·0002 grm. nitrogen to 0·0010 grm.; in all cases within the limit of experimental error.

Recommendations.

I would recommend that the present official methods be continued for the coming year, but modified to include the use of 2 grms. of zinc sulphide and 1 grm. salicylic acid, instead of the 2 grms. zinc dust and 2 grms. salicylic acid, where duplicate determinations of nitrogen are made in fertilisers containing nitrates. My reasons for this are as follows:—

1. The results reported by this method are quite as satisfactory as by the official method.

2. The zinc sulphide can all be added at once, and is, therefore, much less troublesome than the zinc dust.

3. The oxidation is more rapid, and owing to the fact that less salts are present the distillation is more quiet.

I would suggest, not as an improvement of the official methods, but in order to facilitate work and save expense, (1) that the digestion and distillation be performed in the same flask; (2) that metallic mercury be used instead of the mercuric oxide.

ILLUMINATING FLAMES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S.

Flame has always had an attraction for us which has been rivalled by few other natural phenomena; and whether we look back to the times when the old Fire Worshippers treated it as a deity, or take the present century and trace the work which has been done and the discussions which have been held as to its cause, and the actions which render it luminous or destroy its light-giving power, we are fain to admit that a subject which has drawn to it so much attention for upwards of twenty centuries must be a worthy object for research, until such time as we have mastered every detail that bears upon the subject. It is upon flame that we have, up to the present, always depended for artificial illumination; and whether that flame has been derived from the torch, the rushlight, candle, oil-lamp, or coal gas, it has played a part second to none in our domestic comfort; while with the birth and development of coal gas in the early years of this century, flame became an important commercial factor in the history of the country. It was not until the waning years of the last century that Lavoisier's historical researches upon combustion gave us the key to the action which leads to the formation of flame; and since that time its history has teemed with important researches, and still more important applications, which have to-day borne fruit in the improvements we see on every side in our methods of utilising flame for both heating and illuminating purposes.

Flame, be it luminous or non-luminous, is produced by the combustion of gaseous matter; and a moment's consideration will render this clear to our minds. Take a piece of Wallsend or Silkstone coal and note how it burns on the hearth,—first swelling and giving out tarry vapours, which ignite and form jets of flame; and these, encircling the coal, carry on the action, and give us the bright mass of flame which renders our English hearth so cheery a companion. On the other hand, take the coke which is derived from this same coal by its destructive distillation in the gas-retort, and watch the clear coke fire as it burns. Here you have no flame of the kind given by the coal, but simply the glowing mass of fuel, with, at most, a small blue lambent flame playing over its surface.

* A Lecture delivered at the London Institution, February 18th.—From the *Journal of Gas Lighting*.

What is it that has happened during the conversion of the coal into coke which made so great a difference in its method of combustion? If we analyse the coal and then the coke formed from it, we can at once trace the cause which has given us in the one case flame and in the other none :—

	Silkstone coal.	Coke from Silkstone coal.
Carbon	79·0	89·0
Hydrogen	5·2	1·0
Nitrogen	1·5	1·0
Sulphur	1·5	1·2
Moisture	4·0	1·2
Ash	2·8	5·2
Oxygen	6·0	1·4
	100·0	100·0

The conversion of the coal into coke has been accompanied by the elimination of hydrogen, which, partly free and partly in combination with carbon, has been driven off, and has formed the coal gas; and with the destruction of the constituents capable of forming gas the property of burning with flame has disappeared. Again, take a piece of pine-wood and ignite it. Its combustion will be marked by a large and luminous flame; while after conversion into charcoal, by elimination of its gas-producing constituents, it burns with a flameless combustion. From such experiments as these we are forced to the conviction that flame is gas or vapour undergoing combustion; and inasmuch as combustion is chemical combination, we can define flame as being gaseous matter undergoing active chemical combination.

In all the earlier experiments with flame and with the other phenomena of combustion, it was only those substances which ordinarily burnt in air that were studied and experimented with,—those bodies which would burn in air being called combustibles; while oxygen and air were looked upon as supporters of combustion. This conventional limitation of the processes of combustion still exists. A little reflection, however, shows us that such terms must be purely relative; as, if flame depends merely upon active chemical combination taking place between gases, it can only exist where both the combining gases are present, and it cannot matter which of them has the credit of being the combustible, as a jet of air or oxygen will burn just as well in an atmosphere of coal gas or hydrogen as the hydrogen or gas would in air.

It might be imagined that, having come to these conclusions with regard to flame, it would be a comparatively simple matter to solve the other problems connected with it; but on studying the subject it is at once found that the physical and chemical actions taking place are of the greatest complexity, and are in many cases governed by laws of which we know but little. In the propagation of flame, for instance, the combination of the inflammable constituents at the first moment of combustion gives rise to a great increase in temperature, which in many cases is sufficient to check and alter the combination, and in some instances even to cause dissociation of the products formed in the earlier phases of combustion; so that the combination seems to take place in waves, and not evenly, as one might at first imagine, with the result that the maximum temperature of a flame is never so great as one would expect from calculations based on the heat of combustion of the gases and the specific heat of the products and residual nitrogen from the air. These points, together with the rate of propagation and burning of gases, have been the subject of historical researches by Bunsen, Déville, Berthelot, and others; but much still remains to be done before we arrive at any final conclusion on the subject.

By far the most interesting, and at the same time important, chapter in the history of flame, however, is the consideration of the causes which lead to the luminosity of those flames upon which we depend for most of our domestic lighting; and these offer so beautiful a field for both physical and chemical research that they have attracted the attention of many observers, and form no inconsiderable addition to the chemical history of this century. In the year 1816, while engaged upon those celebrated researches which culminated in the discovery of the miner's safety-lamp, Sir Humphry Davy noticed certain facts which led him to work out and propound his theory of the causes which lead to luminosity in flame,—a theory which is generally stated as being that the presence of solid particles in the flame is essential to its luminosity. This theory remained unquestioned until 1868, when Prof. E. Frankland, in his celebrated communication to the Royal Society, showed that, although incandescent solid matter in a flame renders it luminous, luminosity is also in many cases produced when the flame contains very dense vapours at a sufficiently high temperature, and also that a non-luminous flame may be rendered luminous by increasing the pressure.

This gave rise to a storm of criticism, and the next few years drew forth a rich crop of papers on the subject. Prof. Frankland not only showed that flames might be luminous without containing solid particles, but advanced the theory that the luminosity in the flame of a burning gaseous hydrocarbon was due to dense hydrocarbon vapours, and pointed out that the soot deposited upon any cool substance held in such a flame contained hydrogen. To this W. Stein replied, showing that the deposited soot contained less than 1 per cent of hydrogen, which was therefore probably only occluded by the carbon; and also that, if it had been present as a vapour in the flame, it ought, on being heated to the same temperature as the flame, to be once again volatile, which it undoubtedly is not. In the year 1874, Soret attempted to show that the cause of luminosity in flame really does depend upon the presence of solid particles by focussing the sun's rays upon a luminous flame, and examining the reflected light by means of a Nicol prism; and rather later Burch pursued the same line of research, but employed the spectroscope for his examination of the reflected light. Their results point unmistakeably to the presence of solid particles; and at the present time I think there is very little doubt in anyone's mind that, as far as the flames of candles, oil, and gas are concerned, Sir Humphry Davy's theory is the correct one. Indeed, I am strongly of opinion that, although in certain points Davy went a little too far in his theory, had he been still among us we should have found that, in his own mind, he applied his theory more especially to the flames of our ordinary illuminants, as in his original memoir he speaks of "common flames," and distinctly says that "when in flames pure gaseous matter is burnt, the light is extremely feeble," and again, "the intensity of the light of flames depends *principally* upon the production and ignition of solid matter."

While this war of solid particles *versus* dense vapours was raging, Hilgard, Landolt, Blochmann, and Heumann were trying to trace the chemical actions taking place in various flames, and the causes which led to loss of luminosity when air was mixed with coal gas before combustion in the Bunsen burner. Heumann added the further proof to the "solid particle" theory of luminosity, that all flames which owe their luminosity to incandescent solid matter give definite shadows, while those in which luminosity is due to dense vapours give none; and that candle, oil, and gas flames all cause well-defined shadows.

This brings the work done upon the cause of luminosity down to the present time. The accepted description of a luminous flame now is that it consists of several zones,—an inner one, in which no combustion is taking place; a central one, in which, either by selective combustion or by direct decomposition by heat, carbon or very dense hydrocarbons are liberated, and, being heated to incandescence at the moment of production by the combustion of other gases present in the flame, give it luminosity;

and an outer one, which consists of the products of combustion and atmospheric air heated to incandescence, and in which combustion is complete.

The work of Soret, Burch, and Heumann proves beyond doubt that our ordinary illuminating flames contain in the luminous zone particles of solid matter; and the only solid which could be present is carbon, either pure or containing the merest trace of hydrogen. The chief question now remaining to be solved, consequently, is the action taking place which leads to the formation of the solid particles in the luminous zone of the flame. During the last two years I have devoted a very considerable amount of time and attention to the study of this subject, and I think I have found the key to this important problem,—important from a practical point of view, because, until it is thoroughly solved, all efforts to improve our illuminating gases and the burners in which we consume them can only be the outcome of experiments made without definite idea of the means to employ in order to obtain the results we desire.

Coal gas is a mixture of hydrocarbons with hydrogen and small quantities of carbon monoxide, and it also contains traces of carbon dioxide, nitrogen, and oxygen. The gas manager, however, does his utmost to eliminate the last three, which, if present in anything but the merest traces, would seriously injure the illuminating value of the gas. An analysis of the South Metropolitan Company's gas gives the following as its composition :—

Hydrogen	57·08
Hydrocarbons—	
Unsaturated (containing 0·035 p.c. acetylene)	4·38
Saturated	33·99
Carbon monoxide	2·63
Carbon dioxide	0·79
Nitrogen	0·96
Oxygen	0·15
Bisulphide of carbon	0·02
	100·00

The unsaturated hydrocarbons consist of ethylene, benzene, propylene, butylene, and acetylene, and probably also traces of crotonylene and others; while the saturated hydrocarbons consist chiefly of methane, with traces of ethane, propane, and butane.

Analyses made by Landolt of gases withdrawn from various parts of a luminous coal gas flame, and also a long series of analyses which I have made show that as the gas leaves the burner the hydrogen is the first to be consumed; and that, in the passage up the non-luminous part of the flame, the carbon monoxide largely increases in quantity, while at the same time the methane rapidly decreases, and the unsaturated hydrocarbons seem to be the least affected. In the luminous zone the unsaturated hydrocarbons rapidly disappear, while the carbon monoxide formed in the inner zone, and also the residual hydrogen and methane, undergo combustion. Professor Smithells, in a paper read before the Chemical Society in December last (*Journal of Gas Lighting*, p. 68), also proved that during the incomplete combustion taking place in the inner cone of a Bunsen flame, this same increase in the amount of carbon monoxide was to be observed. The fact that the decrease in quantity of the unsaturated hydrocarbons was but slow in the inner zone, and then took place with considerable rapidity in the luminous zone, favoured the theory that they were broken up by heat in that portion of the flame and liberated the carbon, which, by its incandescence, gave the luminosity. But it does not seem to have occurred to anyone to try to determine whether the unsaturated hydrocarbons at the top of the non-luminous zone were of the same description as those of the coal gas.

It is a matter of common observation that the checked combustion of a luminous flame at once gives rise to the escape of acetylene, and also that, if a Bunsen burner catches light at the bottom, large quantities of acetylene are formed, of which the presence is at once detected by its distinctive and pungent odour. These facts suggested the idea that, in the inner cone of the flame, acetylene might be formed by decomposition of the original hydrocarbons; and experiment at once showed this to be the case. Of the unsaturated hydrocarbons present in coal gas, 0·8 per cent consist of acetylene; while at the top of the non-luminous zone of a flat flame produced from the same gas, between 80 and 90 per cent of unsaturated hydrocarbons present consist of acetylene; and in all the other luminous flames experimented with the same action was found to take place.

On taking the most important hydrocarbons present in the coal gas, mixing them with about 20 per cent of air, and passing them through a tube heated to the temperature existing near the top of the inner non-luminous zone, the following results were obtained :—Methane gave rise to unsaturated hydrocarbons, acetylene, and carbon monoxide; ethylene gave acetylene and carbon monoxide; hydrogen charged with benzene vapour gave the same; and ethane gave unsaturated hydrocarbons, acetylene, and carbon monoxide. These experiments clearly show that in the inner non-luminous zone of the flame, the heat generated by combustion of the hydrogen of the coal gas in the presence of the small proportion of air drawn into the flame at this point, causes the conversion of the hydrocarbons present in the gas into acetylene and carbon monoxide.

Acetylene is a clear colourless gas, with a strong and disagreeable odour. It consists of 24 parts by weight of carbon, combined with 2 parts by weight of hydrogen. It is one of those bodies which, during their formation, take in heat instead of giving it out; and it is therefore called an "endothermic" compound. Such substances are especially liable to decomposition, as this is accompanied by a rise in temperature instead of, as is the case with most decompositions, an absorption of heat. Acetylene is decomposed at a bright red heat into carbon and hydrogen, together with traces of tarry matter as well as ethylene; while Berthelot has shown it to be so unstable that it can be broken up into carbon and hydrogen by detonating a percussion cap in it.

These important points being established, it is necessary to ascertain if the temperature existing in the various parts of a flame give any clue to the actions going on within them. The beautiful platinum and platinum-rhodium thermo-couple devised by M. Le Chatelier, and introduced to us by Mr. W. Chandler Roberts-Austen, gives a means of measuring the temperatures of flames with an ease and comparative accuracy which was never before hoped for. I made a small thermo-couple of platinum and 10 per cent of rhodium, platinum wire, using it as thin as possible to reduce errors from loss of heat by conduction, and keeping the wires of considerable length to prevent any chance of rise of temperature introducing conflicting currents at the connections with the galvanometer wires. A reflecting galvanometer was employed, and sufficient resistance was introduced into the circuit to keep the spot of light upon the scale at the highest temperature of the flame; and the scale was then graduated for temperature by taking water at 0° and 100° C., and checking the higher temperature by the fusing-points of the chlorides of the alkalies and alkaline earths, as determined by Dr. Carnelley.

(To be continued.)

A New Thermometer Scale.—F. Salomon (*Zeit. fur Angew. Chemie*).—In this scale the initial point is −273° C., the so-called absolute zero, the freezing-point of water = 100, the intermediate space being divided into 100 equal parts. The writer, like the *Chem. Zeit.*, points out that the proposed new scale has great defects, whilst its alleged advantages are partly unimportant and partly altogether illusory (1° S = 2·73° C !).—*Zeit. Anal. Chemie.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

February 18th, 1892.

Professor W. A. Tilden, F.R.S., Vice-President, in the Chair.

It was announced that the following changes in the Council were proposed by the Council:—

As Vice-Presidents: Mr. A. Vernon Harcourt, F.R.S., and Professor W. Ramsay, F.R.S., *vice* Professors G. Carey Foster, F.R.S., and J. Emerson Reynolds, M.D., F.R.S.

As ordinary members of the Council: Professor Harold Dixon and Messrs. R. J. Friswell, John Heron, and W. P. Wynne, *vice* Dr. E. Atkinson, Professor E. Kinch, Mr. Boverton Redwood, and Professor Thomas Purdie.

Messrs. Holland, Crompton, Bernard Dyer, and T. S. Dymond were appointed to audit the Society's accounts.

Certificates were read for the first time in favour of Messrs. Alexander Barratt, Bronhenlog, Mostyn, N. Wales; Frank Comyns, B.A. 55, South Street, Durham; Joseph Davies, 28, Robarts Road, Anfield, near Liverpool; James C. Frazer, Victoria Square, Adelaide, South Australia; John Theodore Hewitt, St. John's College, Cambridge; William James McKerrow, care of Hall, McKerrow, and Co., Nicholas Street, Manchester; George Harry Major, Coldstream Street, Llanelly; Reginald Edensor Stanley Richardson, Elmfield, Knighton, Leicester; Thomas Shortridge Tweedie, The Moat, Annan; George Isaac James Wells, F.I.C., Kinderton Lodge, Middlewick, Cheshire.

The following were duly elected Fellows of the Society:—Arthur Adams; Frederick Edward Adams; Frederick Fielding Bond; William John Atkinson Butterfield; Hugh Brown Collins, B.Sc., C.E.; Francis V. Darbishire; Robert Brooke Floris; Alfred Thomas Gailleton; William Percy Hatton; James Hendrick; John C. Hewlett; Lionel Manfred Jones; Albert Henry Luckett; William Cossar Mackenzie; John Edward Whitley McFall; Charles Stephen Meacham; James Hill Millar; Robert Ludwig Mond; William Shields Myers; William Pullinger; Ernest John Parry; Charles Frederick Seymour Rothwell; Thomas John Buckler Sandercock; James Alexander Schofield; Thomas Skurray; George P. Darnell Smith; Henry John Spray; Alfred James Squires; James Sykes; Morris William Trewers; Hugh Woods.

The following papers were read:—

108. "*A Search for a Cellulose-dissolving (Cytohydrolytic) Enzyme in the Digestive Tract of certain Grain-Feeding Animals.*" By Horace T. Brown, F.R.S.

The author, in a recent paper by himself and G. H. Morris (*C. S. Trans.*, 1890, 459), has shown that during germination of the seeds of the grasses the cell-membrane of the endosperm is broken down and destroyed by a specific cellulose-dissolving enzyme, or *cytohydrolyst*; and that the breaking down of the cell-wall is a necessary preliminary to the dissolution of the reserve starch and proteids of the cell contents, which otherwise would not readily come under the influence of the extremely indiffusible starch and proteid-dissolving enzymes secreted by a certain layer of cells in the embryo.

As it was found by the author that the analogous starch-hydrolysing enzyme of animal saliva and of the pancreatic secretion experiences the same difficulty in traversing the thin cell membrane, it appeared almost certain that in grain-feeding animals there must be some provision in their economy for removing, during the processes of digestion, the inverting cell-membrane of the starch-containing cells of the interior of the grain, and of thus bringing the cell contents fully under the influence of the digestive enzymes of the alimentary canal.

An examination of the contents of the small intestine of a pig, fed a few hours before death with barley-meal, conclusively showed that by the time the food had reached this point the originally intact parenchymatous cell walls of the grain had undergone almost complete dissolution, and that the starchy and proteid cell-contents had been completely freed from their cell envelopes and were being rapidly dissolved under the influence of the pancreatic secretion.

As the phenomena were in the highest degree suggestive of the cell wall being dissolved by an enzyme, the search for this cytohydrolyst was commenced by a very full examination of the *pancreas*, that of the *pig*, *horse*, *ox*, and *sheep* being employed, but not the slightest evidence could be obtained that this organ is capable of secreting an enzyme having any action on cellulose.

A continuance of the search in the small intestine itself, which is known to possess certain hydrolysing functions, was rendered unnecessary when it was discovered that the action on the cell wall of the grain food has already taken place before the stomach contents have passed into the small intestine. It was, therefore, in the stomach itself, or in the salivary glands, that the search had to be continued; but the enquiry was further narrowed by the fact that animal saliva was found to be incapable of exercising any action on cellulose.

The experiments on the stomach membrane and stomach contents were all made on the *horse* and the *pig*. The dissolution of the vegetable cell membrane in the stomach may be due to one or more of the following causes, viz.:—

1. To mechanical disintegration brought about by the "churning" and "propulsive" movements of the stomach during digestion.

2. To the action of the natural acids of the stomach, which may bring about the dissolution of the cellulose either (*a*) by direct hydrolysis, or (*b*) by converting a zymogen of the grain into an active cytohydrolyst.

3. To the action of a special enzyme secreted by some portion of the mucous membrane of the stomach.

4. To the direct or indirect action of living *micro-organisms*. These may break down the cell wall by:—

(*a*). A direct attack of the living organism without the intervention of a secreted enzyme.

(*b*). A previous secretion by the organism of a special cytohydrolyst.

(*c*). An indirect production of a cytohydrolyst by the modification of some of the constituents of the grain by the vital processes of the micro-organisms.

5. To the self-digestion of the food under the influence of a cytohydrolyst pre-existent in the grain before ingestion.

Each one of these possible cases had to be examined separately in order to determine the *vera causa* for the destruction of the parenchymatous cell wall which undoubtedly takes place in the stomach during digestion. It is shown by numerous experiments that the destruction of the membrane is not due to mechanical disintegration nor yet to any action of the stomach acids, nor is it attributable to the direct or indirect influence of micro-organisms. The cell wall is, undoubtedly, dissolved by a cytohydrolytic enzyme; but, contrary to what was expected, this enzyme is not secreted by any portion of the mucous membrane of the stomach, but is pre-existent in the grain before ingestion, the animal itself contributing nothing to the result except by affording suitable conditions of temperature, &c., for the action of the enzyme.

In a previous paper by the author and G. H. Morris (*loc. cit.*) it was stated that the cellulose-dissolving enzyme which is of so much indirect importance to the plantlet during the germination of the seeds of the grasses is not pre-existent in the seed during its resting stage, but is a

product of the germinative processes. Although this is strictly true as regards the morphologically perfect and highly-matured barley which was used during the greater part of that research, it is not strictly true of all barley or grasses, especially of barley grown in this country under somewhat imperfect climatic conditions. This, as a rule, contains even in its resting state more or less of the cellulose-dissolving enzyme, and the same is true as regards *rye*. In *oats* the cytohydrolyst is particularly abundant, and this fact explains the very great rapidity with which the endosperm of the oat is disintegrated in the early stages of digestion in the horse as observed by the author, and also throws considerable light on the cause of the high estimation in which oats are held as a food-stuff.

That the dissolution of the cell membrane is due wholly and entirely to the cytohydrolyst of the food-stuff was proved by making a parallel series of experiments on animals fed in the one case with barley-meal which was destitute of cytohydrolysing power, and in the other case with the same meal to which a small amount of germinated grain had been previously added. In the first instance no destruction of the parenchymatous cell wall took place in the animal's stomach; whilst in the second case the vegetable membrane was completely dissolved in a very short time.

The presence of a cytohydrolyst and its amount in the food of grain-feeding animals is a factor, and, perhaps, a very important one, in their nutrition, for the more or less complete preliminary preparation of the food in the stomach before it passes into the intestine cannot be a matter of indifference to the animal physiologically.

The experiments have a very important bearing on the lengthy investigation carried out at Rothamsted, some years ago, on the relative value of malted and unmalted grain as a food for stock. The whole of the subject requires re-examination from a new point of view, and it does not seem at all unlikely that the supposed condimental value of malt, which has been insisted on by many agriculturists in the face of the Rothamsted experiments, may, after all, be a fact.

Discussion.

Mr. BROWN, in reply to Professor Tilden, said that the enzyme in question was undoubtedly distinct from diastase and unable to attack starch. With reference to the question put by Professor Green, whether the cæcum of herbivora was not the seat of the digestion of the cellulose in the major portion of their food, he thought that it was clearly shown by Tappeiner's experiments that this was the case, and that its digestion was effected through the agency of micro-organisms. He was unable at present to give any reply to Mr. Cross's question as to the behaviour of the different varieties of cellulose.

109. "*On the Influence of Oxygen and Concentration on Fermentation.*" By ADRIAN J. BROWN.

The author describes experiments on the reproductive power of yeast, from which it appears that all fermentable nutritive solutions encourage the increase in number of yeast cells, to some fixed point beyond which they will not reproduce themselves; and he shows that if a greater number of cells be introduced into a fermentable liquid than the liquid could originally develop, no increase in number of cells takes place. As under conditions like these fermentation still proceeds vigorously, a number of disturbing factors which complicate the results obtained under ordinary conditions may be eliminated by using non-multiplying yeast cells.

A series of experiments are described in which fermentations were conducted in presence of large amounts of oxygen, whilst at the same time duplicate experiments were made in which oxygen was excluded; the same number of non-multiplying yeast cells being used in both cases, and all the other conditions, such as temperature, agitation, &c., being kept constant. Under these circumstances it was found that both equal numbers of yeast cells and equal weights in presence of oxygen exercised more fermentative power than when unexposed to its influence. The author is unable to reconcile these results with M. Pasteur's theory of fermentation.

Experiments carried out with a fixed number of non-increasing yeast cells also showed that the amount of sugar fermented in a given time by them did not depend on the concentration of the solution, but that within the limits of 20 and 5 per cent solutions of dextrose, approximately the same weight of sugar was fermented. When the strength of a solution reaches 30 per cent of dextrose fermentation proceeds much more slowly.

110. "*Limettin.*" By WILLIAM A. TILDEN, D.Sc., F.R.S.

Limettin is the name given by the author to a crystalline substance deposited from the essential oil of the lime, originally described by him in conjunction with C. R. Beck (*C. S. Trans.*, 1890, 323).

Further investigation of its properties shows that, instead of the formula $C_{16}H_{14}O_6$ first attributed to it, limettin has the composition expressed by the molecular formula $C_{11}H_{10}O_4$, which requires nearly the same percentages of carbon and hydrogen.

By the action of nitric acid it is converted into a nitro-derivative $C_{11}H_9(NO_2)O_4$, and by the action of bromine into a dibromo-derivative $C_{11}H_8Br_2O_4$, while chlorine converts it into a trichloro-compound $C_{11}H_7Cl_3O_4$. The dibromo-compound also exchanges the third atom of hydrogen for chlorine, giving $C_{11}H_7Br_2ClO_4$. Oxidising agents convert limettin into acetic or oxalic acid without definite intermediate products. Potash fusion produces from it phloroglucol and acetic, but no other acid. Treatment with concentrated solution of hydrogen iodide causes the elimination of two methyl groups.

Sulphuric acid slightly diluted causes limettin to assimilate a molecule of water forming a phenolic compound of which the diacetate was prepared and analysed.

Limettin is not attacked by acetyl chloride, by phenylhydrazine, or by sodium amalgam, and it gives no colouration with ferric chloride. It forms very pale yellow thin prisms, which melt at 147·5; it dissolves in alcohol, benzene, toluene, and acetic acid pretty freely, but scarcely in water or in light petroleum. Dilute solutions exhibit a beautiful violet fluorescence. It seems to have the constitution $C_6H_3(OCH_3)_2{\cdot}C_3HO_2$. Further experiments are in progress.

111. "*The Acid Action of Drawing Papers.*" By C. BEADLE.

Professor W. N. Hartley has recently communicated a note on this subject (*Proc. C. S.*, 1892, 19) which raises questions of considerable technical importance. The fact of the "acidity" of papers need not be discussed, and Professor Hartley's contention that an acid constituent in the paper has a serious effect on "water-colours" applied to the paper I am not in a position to criticise. I merely wish to point out that the author is probably in error as to the *cause* of the acidity, which he takes to be a residue of sulphuric acid left in the "fibre" (rags) after the process of "souring" and washing.

The mill where the "Whatman" papers are made is situated at Maidstone, and the water used in the manufacture is the characteristically hard water of that district. The "souring" of the rags is followed by a long process of continuous washing in the "engine," and after some years' experience of paper making in the Kentish district I am satisfied that no acid can survive this treatment.

On the other hand, the papers are sized with gelatin and alum, and it is to the presence of the latter constituent that the "acidity" is, in my opinion, due. In a recent examination of one of these papers I obtained, by treatment with distilled water, an exhaust which showed "acidity" equal to 2·3 c.c. normal H_2SO_4 per 100 grms. paper, *using litmus* as indicator in the titration, and yet this exhaust was *basic to methyl orange*. Sulphate of alumina, $Al_2,3SO_4$, being acid to methyl orange, the evidence is

complete that the apparent "acidity" of the aqueous exhaust is due to the presence of a basic sulphate of alumina (*cf. Jour. Soc. Chem. Ind.*, 1891, 202).

OBITUARY.

THE LATE PROFESSOR DITTMAR.

By the death of Professor Dittmar, of Anderson's College (Glasgow and West of Scotland Technical College), the world of chemistry and physics has suffered a great loss. Since he first came among us some thirty-three years ago, at the invitation of Prof. Sir Henry Roscoe, who, meeting him and recognising his worth in the laboratory of the distinguished Bunsen, invited him to become his private assistant, Wm. Dittmar's name has steadily increased in repute as a worker in, and exponent of, his science. Dying, as he did, literally in harness,—for he left his lecture-room for his death-bed, and calmly summed up the events of his last day with the words, "Well this morning, ill to-night, dead to-morrow,"—even if he had been but a good average man, who did his duty so as to give fair satisfaction, some words of regret and praise would have been not ill-spent by the side of his suddenly opened grave. But the great variety of Prof. Dittmar's labours as a lecturer, analyst, chemical expert in legal cases, writer, investigator, and discoverer; his long enthusiastic devotion to science; his association as a collaborateur with some of the most distinguished British chemists; his influence on the many promising young chemists trained after his methods; not to mention his striking individuality and sterling worth as a man, all call for a hearty tribute of admiration and respect to his memory and of sympathy with his family.

Born in Umstadt, near Darmstadt, in 1833, which latter town has been the birthplace of Liebig, Strecker, Kekulé, and Schorlemmer, Wm. Dittmar meant at first to follow the profession of a pharmaceutist, but eventually entered in 1857 the laboratory of Bunsen, who soon offered him an assistantship.

Sir Henry Roscoe having, as already mentioned, here asked him to assist him, took Mr. Dittmar with him to Manchester. In 1861 he became chief assistant to Sir Lyon Playfair, and in this way became the teacher of Prof. Dewar, whose respect and friendship for his old master has been all along warm and pronounced. Until 1869 he was well known to Edinburgh students as embodying the enthusiasm, abstraction, and untiring devotion to work understood to be characteristic of the typical German Professor, but all held him in honour for his high character, simple kindly nature, and marked abilities. It was to everybody's satisfaction that after three years in his native country spent in the work of "Privat Docent," at Poppelsdorff, where, we believe, he delivered a course of lectures on meteorology, he preferred to refuse a chair at Cassel, and to accept in 1872 his old post at Edinburgh under Prof. Crum-Brown, with whom there was thus renewed a deep friendship. About a year afterwards Mr. Dittmar was appointed to the newly-instituted Chair of Practical Chemistry in Owen's College, but returned to Scotland in 1873 to occupy that of Chemistry in the Andersonian University of Glasgow. Every one knows that this Chair has been long remarkable, rather for the celebrity of its occupants than the worth of its emoluments.

Prof. Dittmar found in the Anderson's College a sphere not uncongenial to him. The day was past when one might hope to reimburse himself for his efforts so well as the popular and brilliant Penny did, but Dittmar set himself steadfastly to sustain the tradition of fame which Graham's genius had gained, and Ure's great repute as an industrial chemist had maintained in Anderson's College. He felt, moreover, and acknowledged the competence of Thorpe whom he succeeded. How successfully he upheld the repute of his Chair his wide popularity as a lecturer has attested. The laboratory-roll from small beginnings rose to sixty-three, and has for years averaged fifty; an increase which, be it observed, scarcely anyone will be disposed to deny arose from Prof. Dittmar's great personal reputation as a laboratory trainer. The men who have been thus trained are at one in viewing his influence and power as a teacher as quite extraordinary,—an estimate which may take its complexion from daily contact with a nature so kindly and cheerful, a critical power so genially trenchant, and knowledge and fertility of resource so vast as those of Prof. Dittmar, but which is substantiated by a perusal of the various manuals of instruction that bear his name.

It is not out of place to mention shortly the chief publications in which Prof. Dittmar has made known his views and the results of his research.

His contributions to chemical literature have been very numerous as well as voluminous, and anyone who has read them will be struck with the freshness of illustration, the mastery of detail, the clearness of statement, and the well balanced method with which they are written. In proof of this we may single out the article "Analysis," in the Second Edition of "Watts's Dictionary of Chemistry"; the article on "Fermentation" in the "Encyclopædia Brittanica," New Edition, and a masterly article of marked individuality on the "Atomic Theory" in the "National Cyclopædia." The substance of this last, if we mistake not, was originally part of a projected but only partly completed work on organic chemistry, and it lies alongside of a contribution to the Royal Society of Edinburgh (1878), in which he expresses his belief that the true way to demonstrate Dalton's law of multiple proportions is to represent it as a necessary corollary of the assumption of the atomic theory with Avogadro's supplement.

To the "Encyclopædia Brittanica," New Edition, Prof. Dittmar contributed also the important articles on metals and metallurgy, the potassium metals, the platinum metals, besides briefer ones on silver, nickel, mercury, manganese, magnesium, tin, titanium, lanthanum, tungsten, molybdenum, lime, sulphur, selenium, silicon, &c.

Besides occasional articles of an industrial character, such as those on "Alkali Proof Vessels" and "Tension Thermometers and Pyrometers," in the *Jour. Soc. Chem. Ind.* (1884 and 1885), he contributed regularly to the *Chemische Industrie*. Before the Royal Society of Edinburgh he laid at least three extensive researches:—

1. Dittmar and Fawsitt, May, 1887, "Contribution to our Knowledge of the Physical Properties of Methyl Alcohol."

2. Dittmar and MacArthur, July, 1887, "Critical Experiments on the Chloroplatinate Method for the Determination of Potassium, Rubidium, and Ammonium; and a Re-determination of the Atomic Weight of Platinum." At the close of this very satisfactory research he fixes this last as not far from 195·5, and holds that to agree well with Seubert's result.

3. June, 1889, "On the Behaviour of the Hydrates and Carbonates of the Alkali Metals, and of Barium at High Temperatures; and on the Properties of Lithia and the Atomic Weight of Lithium."

In 1884 was published Prof. Dittmar's report "On the Composition of Ocean Water," which formed part of the treasure given to science by the famous *Challenger* Expedition of 1873—1876. To the seventy-seven waters, of which the report furnishes a complete analysis, he did the utmost justice. The task, as he carried it out, was colossal, but not more so than his patience and indefatigability. It seemed, as the critic in *Nature* puts it, "more like a life-work than that of six years." How largely and ably both mathematics and physics were laid under contribution to obviate probable error,—with how much foresight, caution, and ingenuity the work was

carried on, can only be quite understood by a careful consideration of the full report, but some idea may be got by reading the digest in which Prof. Dittmar summarises his *Challenger* work for the benefit of the Philosophical Society of Glasgow (December, 1884).

He concludes that free CO_2 in ocean water is exceptional; that in surface waters, as the temperature falls, the proportion of CO_2 increases, and *vice versa*; and that within equal ranges of temperature the proportion of CO_2 is lower in the surface waters of the Pacific than in those of the Atlantic.

Setting out in the track Forchhammer pursued in 1864 Dittmar outstripped him, and is to be regarded as our final authority for considering that while the salinity of the ocean is variable, the relative proportions of the salts are practically balanced. But upon these results Prof. Dittmar did not plume himself, saying expressly that "whatever may be the merits of his work, its better part consists of critical investigations into old, and attempts at inventing new, analytical processes." Notwithstanding the diffidence with which Prof. Dittmar regarded the value of his work in respect to oceanography, it is universally esteemed to be the greatest published contribution to the chemistry of ocean-water, and, as such, is a public as well as a scientific service of the highest merit. Pre-eminently fitted by his nature, experience, genius, and opportunities to test by re-trial and modification the results of earlier great workers, Prof. Dittmar, with the co-operation of Mr. J. B. Henderson, undertook an investigation of the "Gravimetric Composition of Water," given to the Philosophical Society of Glasgow, December, 1890. This, as all know, to be worth anything, entailed work of the severest kind, and could only be a labour of pure love for chemical science.

It is impossible, without reading the detailed account of the research, to grasp the closeness of the criticism applied to Dumas' work, or the ingenuity with which its defects are accounted for and remedied. Dumas' neglect of "vacuum corrections," Erdmann's and Marchand's misplaced trust in the perfect drying power of fused chloride of calcium, Dumas' method-error, owing to atmospheric air in his hydrogen, the suspected and proved production of water by the action of hydrogen on hot glass, and the unexpected discovery that, even in the cold, hydrogen acts on oil of vitriol so as to give sulphurous acid; these and, indeed, the whole of the details, are not merely deeply interesting, but present to all who aim at research a lesson of the highest kind. It would have been strange indeed had not such a labour been in part repaid with the Graham Medal.

In all these investigations, whether undertaken for fee or for love's sake, the outstanding characteristics of Prof. Dittmar were such as did him honour not merely as a scientist but as a man. He was not merely a close reasoner, a happy adapter, a severe critic of himself as well as of others, a man of immense fertility and resource, willing to "toil terribly for truth's sake," but he showed in the self-estimate of his work great modesty and candour; in regard to the honest and ably done work of others a due respect, even when their results are opposed to his own; and a scrupulous care in acknowledging the aid and services of all his coadjutors.

"Being," says he at the close of his last research, "an incorrigible 'Proutian,' I do not give up the hope that the true number may be 1 after all;" and though he finds his result 1·0085 in the good company of Stas, Cook and Richards, Noyes and Rayleigh, he says "these five investigations might be said to settle the question were it not for Keiser, who finds 1·0032, and it is impossible to pass over *his* research!"

Besides being, as a theorist, the first to correctly interpret the dissociation of a solid substance and the author of the line of researches we have noticed, his memory has claims upon the respect of all laboratory workers as a high authority on precision-balances, a subject which he treats in "Thorpe's Dictionary" and elsewhere. His "*microscale*" and "*auxiliary gravity-bob*," as made by Oertling and Staudinger, have been of great value in saving time and ensuring accuracy in weighing; and besides many improvements in processes and apparatus, his "*differential method*" of determining specific gravities of liquids is the most perfect known.

Professor Dittmar gave years ago to the world several works of a more purely academic character: a "Manual of Qualitative Chemical Analysis," of great erudition; an elementary book on "Analytical (Qual.) Chemistry;" and "Tables to Facilitate Chemical Calculations." More lately he published a book on "Quantitative Chemical Analysis," which, replete with fresh, well-chosen, well-arranged material, and thoroughly abreast of the latest improvements in processes, contains what has been hailed in all quarters as a most admirable exposition of the principles and practice of gas analysis. This work, and the unique and in great degree original first part of the "Chemical Arithmetic," more lately published, stand evidence of Dittmar's greatness as a teacher.

All who read his books, all who worked under his guidance, all who listened to his lectures, felt convinced that in him there was no mere compiler, no retailer of second-hand thought, but a mind of rare scientific attainment and insight unremittingly at work. "Brain sucking"—to use his own strong expression—he despised, as likewise the degrading of great intellectual powers to mere money-making. Genial, simple, lovable, he was the staunchest of friends, and the most resolute of opponents. He could only view things from what he thought the stand-point of right—never from that of expediency.

He remained unspoiled by the honours which came to him in later years, and his dislike to parade himself at conferences may probably explain why so few of his chemical *confrères* know intimately the manner of man he was. We may fittingly apply to himself the words he utters in a short but admirable sketch of the great Wöhler and his work: "One student might wish to work on organic chemistry, another on minerals, a third on metallurgy, a fourth on rare elements; let them all go to Dittmar, and they all, like the fifth or sixth, would find themselves in the right place!" Equally appropriate to himself is the well-pleased reflection with which he closes the sketch: "He continued working to almost the edge of his grave."

CORRESPONDENCE.

THE DIRECT COMBINATION OF CHLORINE WITH METALS.

To the Editor of the Chemical News.

Sir,—In the last number of the Chemical News (p. 101) is an article with the above heading by U. Kreusler. The author would appear to be somewhat surprised that dry chlorine had no action on brass wire.

Twenty-eight years since I patented a process for purifying bone-black, in which it was shown that, while dry chlorine gas or dry hydrochloric acid gas would combine with the dry carbonate of lime deposited in the bone-black during the sugar refining process, it had no action whatever on a much more soluble substance than brass, viz., the dry tribasic phosphate of lime of the bone-black.—I am, &c.,

Edward Branes.

Moatlands, Paddock Wood,
Feb. 29, 1892.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

Sir,—The reply inserted in your last issue (p. 106) to the letter of your correspondent "W. S." will, I think, be a

very disappointing one to the Society of Students. It is all very well for "C. O. O." to say, "Seek first the Science and its discipline and all those things shall be added." It seems to me that "C. O. O." has not thoroughly grasped the idea intended to be put forward by "W. S." Chemistry is such an extensive science that one cannot hope, even with the hardest study, to excel in every branch of it. Very few men thoroughly qualified for the position of chemist in a works are competent to teach a class of students who, in their turn, intend to become teachers of the pure science.

Between the branches of chemistry (as divided by Mr. F. Woodland Toms, in his letter at p. 105), viz., the analytical chemists in works, the analyst pure and simple, and the professor who is open for consultation there is a wide difference, and the point to be discussed is which of the branches is likely to be most beneficial to a student. —I am, &c.,

F. G. M.

Manchester, Feb. 29, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 7, February 15, 1892.

A New Method of Organic Analysis.—M. Berthelot.—The method consists in burning the substance under examination in the calorimetric bomb in oxygen compressed to 25 atmospheres. The combustion is complete and instantaneous, contrary to what takes place in combustions by copper oxide. When the combustion is effected the gases are allowed to escape from the bomb through the ordinary system of tubes for organic analysis, a desiccating tube filled with sulphuric pumice, and then tubes with liquid and solid potassa. When this is effected the surplus gases are extracted from the bomb by means of a mercurial pump and caused to pass into the same absorbent apparatus. Purified air is then passed into the exhausted bomb, repeating the operation three or four times so as entirely to extract the carbonic acid. The determination of the carbon may be thus executed with great precision and promptitude. The determination of the hydrogen is rather more complicated. It may be effected by using dry oxygen and by slightly heating the bomb after the operation so as to evaporate all the water in the successive gaseous atmospheres which result from the foregoing operations. But we must take into consideration the traces of nitric acid produced during the combustion and volatilised at the same time as the water. The separate determination of the carbonic acid is not subject to this complication, as the water condensed in the bomb retains entirely these traces of nitric acid. The combustion in the bomb enables us also to determine completely the sulphur of organic matter by adding beforehand 10 c.c. of water; the sulphur remains in the water in the form of sulphuric acid, as we have demonstrated by very precise determinations. This is the most expeditious method for the determination of sulphur and also of phosphorus in organic compounds.

Use of Compressed Oxygen in the Calorimetric Bomb.—M. Berthelot.—Compressed oxygen may be introduced into the bomb in two different manners. It may be drawn from a gas-holder filled beforehand at the ordinary pressure, saturated with moisture, and then compressed in the calorimetric bomb. In this case the entire space is necessarily saturated, and a certain quantity of watery vapour is condensed capable of restoring the saturation at the end of the experiment. As the final temperature is higher than the initial temperature by about 3°, it results that a small quantity of water has been evaporated during the experiment. But this quantity is so small that it does not introduce an appreciable correction. It is different if we make use of a receiver filled with oxygen compressed beforehand at a pression of 100 to 120 atmospheres. Such oxygen is dry or nearly so, and we have in most combustions to take into account the evaporation of the water in the void space of the bomb. This quantity may be neglected in industrial operations but not in strict scientific researches.

Action of the Alkaline Metals upon Boric Acid. Critical Study of the Processes for the Preparation of Amorphous Boron.—Henri Moissan.—The author has examined the boron of Gay-Lussac and Thenard, that of Deville and Woehler, and that of Berzelius, none of which are pure. If we cause an alkaline metal to react upon boric acid the reaction takes place with a great liberation of heat, by means of which the greater part of the boron which had been set free combines with the excess of the alkaline metal, and with the metal from the apparatus in which the reaction has been effected. If we afterwards exhaust the product with water and hydrochloric acid we obtain, after desiccation, a mixture of boron, sodium, and iron borides, boron hydride and nitride, and hydrated boric acid. This is the mixture which has hitherto been regarded as amorphous boron.

Light of a Temporary Star in Auriga.—G. Rayet.—The spectrum of this star consists of a continuous spectrum in which the red and the violet appear very luminous, and of four brilliant bands in the green, the wave-lengths of which are:—No. 1, 518 $\mu\mu$, near *b*; No. 2, 501; No. 3, 493; No. 4, 487, near F, very probably F. The most brilliant of these bands are the second and the third. A more recent observation in the night between February 14 and 15 enabled the author to detect the brilliant line Hα of hydrogen in the red and that of sodium.

Determination of the State of Dissolved Salts according to a Study of their Contraction.—Georges Charpy.—This paper requires the two accompanying diagrams.

On Certain Properties of Bismuthic Acid.—G. André.—If after obtaining bismuthic acid as pure as possible we try to re-combine it with potassa, it is impossible to obtain the neutral salt BiO_3K. The author has previously shown how bismuthic acid is commonly obtained by passing a current of chlorine into a hot concentrated solution of potassa holding bismuth oxide in suspension. In the preparation of bismuthic acid effected either with a bromised solution of bismuth bromide in presence of potassa, or by means of chlorine acting upon the oxide in presence of potassa, a persistent emulsion is produced by prolonged washing. We remark the tendency of bismuthic acid to produce complex bodies by uniting with its own anhydride. Are such compounds truly definite?

On a Definite Barium Carbide.—M. Maquenne.—Barium carbide corresponds to the formula C_2Ba. Its decomposition by water may be expressed by the following equation, $C_2Ba+2H_2O=C_2H_2+Ba(OH)_2$. It is evident that barium acetylide, like the nitride, must play an important part in the synthetic production of the corresponding cyanide.

On the Principles which Accompany Chlorophyll in Leaves.—A. Etard.—The author demonstrates in presence of chlorophyll the existence of a triatomic alcohol, *oenocarpol*, a diatomic alcohol, *vitoglycol*, and a monatomic alcohol, *medicagol*. These new crystalline compounds resemble cholesterine only in their outward appearance.

Transformation of the Aromatic Amines into Chlorohydrocarbides.—M. Prudhomme and C. Rabaut.—The chromic, ferric, &c., chlorides, act like cupric chloride upon diazobenzene chloride. For the reduction

of the nitrates of the aromatic amines, and their transformation into chlorohydrocarbides, we may substitute for cuprous chloride the chromous chloride, which is also a very energetic reducer. The ferrous and stannous chlorides do not determine the reduction of nitrates and transformation into diazo-derivatives.

On the Assimilation of the Carbohydrates.—M. Hanriot.—Glucose introduced into the animal organism does not undergo simply a combustion or a transformation into glycogene, but it is converted quantitatively into fat.

Journal fur Praktische Chemie.
New Series, Vol. xliv., Parts 18, 19, and 20.

Oxidation of Mixed Monocarbonyl Ketones of the Aliphatic Series.—G. Wagner.—The oxidation of the mixed ketones, in which the two atoms of carbon adjacent to the carbonyl are hydrogenised, takes place at 100° generally in two directions, chiefly in that in which the most heat is liberated.

Oxidation of Tertiary Alcohols.—G. Wagner.—The oxidation of the tertiary alcohols consists probably in the hydroxylisation of one of the atoms of carbon directly combined with the group C(OH), whereby the oxidation of such tertiary alcohols in which these carbon atoms are hydrogenised to a different extent and combined with different radicles, probably by the same or similar rules which we have encountered in the ketones.

Researches from the Laboratory of the University of Freiburg.—These consist of the 45th memoir by Ad. Claus on the oximes and the so-called stereo-chemistry. The author contends that these and all the phenomena of isomerism which are known for the production of the transposition of benzil and hydroxylamine may find a simple explanation, as depending upon structural isomerism without the help of any stereo-chemical hypothesis.

Calorimetric Researches by F. Stohmann. 25th Treatise: On the Thermic Value of the Constituents of Nutriment and their Derivatives. — F. Stohmann and H. Langbein.—This voluminous essay with its many tables does not admit of useful abridgment.

Remarks on the Paper by Ad. Claus: "The Transposition of Bibromsuccinic Ester with Zinc."—Arthur Michael.—This discussion is becoming very warm, and A. Michael declares that, as far as he is concerned, it must cease.

Communications from the Chemical Institute of the University of Kiel. No. 11.—These consist of a paper by A. Heuser and C. Stoehr, on methylised dipyridils.

The Bismuth Controversy.—A. Classen replies to the paper of H. R. Schneider (*Journ. f. Prakt. Chemie*, vol. xliv., p. 23). He shows that the bismuth used by Schneider for determining its atomic weight was by no means pure.

On the Translocations of the Propyl Group.—Oscar Widman.—The author does not believe that any doubt exists as regards the translocations within the propyl group of the cymol and cuminic-derivatives.

Some Thio-derivatives of Orthoaminobenzamide.—Andrew Stewart.—A preliminary communication.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xvi., No. 2.

New Mechanical Process for the Continuous Manufacture of Agglomerated Soaps compared with the Present Process.—Jos. Goffin.—The improvements described in this paper are purely mechanical.

Purification of Cupriferous Bismuth.—Ed. Matthey. —From the Chemical News.

MEETINGS FOR THE WEEK.

Monday, 7th.—Medical, 8.30. (General Meeting).
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).

Tuesday, 8th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Medical, 8.30. (Annual Dinner).
—— Photographic, 8.

Wednesday, 9th.—Society of Arts, 8. "Experiments on the Durability of Modern Pigments," by A. P. Laurie, M.A.
—— Geological, 8.
Pharmaceutical, 8.

Thursday, 10th.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
—— Royal Institution, 3. "The Progress of Romance in the Middle Ages," by Prof. W. P. Ker, M.A.

Friday, 11th.—Royal Institution, 9. "Japanesque," by F. T. Piggott.
—— Astronomical, 8.
—— Physical, 5. "Thermodynamics and the Action of Light on Silver," by Mr. H. M. Elder. "On Choking Coils," by Prof. J. Perry, F.R.S.

Saturday, 12th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

Erratum.—P. 102, col. 1, line 17, *for* "1-200th" *read* "1-2000th."

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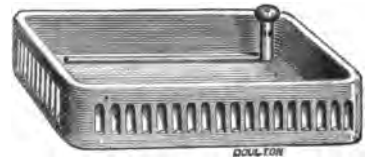

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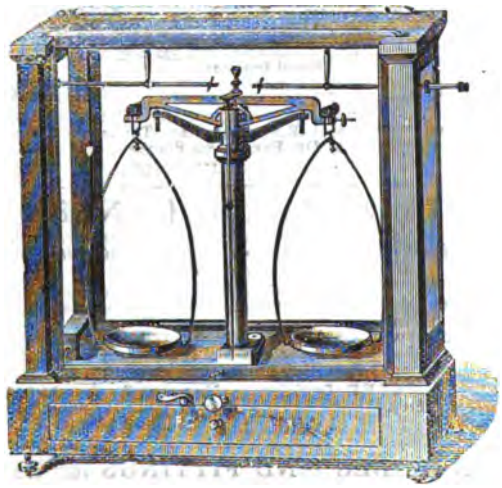

FIG. 34.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1685.

PRELIMINARY NOTE ON NOVA AURIGÆ.*

By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S., and Mrs. HUGGINS.

We have delayed up to the present time presenting any account of our observations of Nova Aurigæ, in the constant hope that fine weather would enable us to make our observations more complete. We think now, however, that it may be of interest without further delay to send a short preliminary notice of this remarkable, and, in some respects, unprecedented, celestial phenomenon. For up to this time we have no record of a star in the spectrum of which the bright and dark lines of the same substances have been regarded as indicating respectively motions of approach and of recession of so great magnitude. It was partly for this reason that we were anxious for the opportunity of observing if any change in the amount of relative motion would show itself.

We received a telegram from Dr. Copeland in the early morning of the 2nd inst., and began our observations of the star on the night of the 2nd inst.

Perhaps the most noticeable feature to the eye in the star's spectrum was the great brilliancy of the hydrogen lines at C, F, and G; but the point of greatest interest was obviously that two of these lines, F and G, and we have since observed the same with C, were accompanied each by a strong absorption line on the side towards the blue. Comparison with the lines of terrestrial hydrogen, while confirming the obvious presumption that the star lines were really those of hydrogen, showed at once a large motion of recession of the bright lines and a motion of approach of a similar order of magnitude of the hydrogen which produced the absorption.

A photograph which we have since taken gives the star's spectrum as far in the ultra-violet as about λ 3200. On this plate we see not only the other hydrogen lines at *h* and H, but also the series beyond, which is characteristic of the white stars, bright, with dark absorption lines on the blue side.

Besides the hydrogen series, there appear to be other lines doubled in similar manner, including the sodium line at D. The line K is strongly impressed upon the plate, but in our photograph is not followed by an absorption so strong as in the case of H, where the absorption may be two to substances.

In the green part of the spectrum three very brilliant lines are seen on the red side of F. One of these falls not far from the position of the chief nebular line; but even when the shift of the spectrum is taken into account, we can scarcely regard this line as the true nebular line. In this connection it was a point of some importance to find that the strong and very characteristic line of the Orion nebula, which falls about λ 3725, is absent in our photograph of the nova, also the strong nebular line between $\alpha\beta$ at about λ 3868. The third line from F is rather broad and resolvable into lines. It falls partly upon the more refrangible pair of the magnesium triplet at *b*, but its character and position do not permit us to ascribe it either to magnesium or to carbon.

We wish to mention an early photograph of this star taken on the 3rd inst. by Father Sidgreaves, at Stonyhurst, which we had the privilege of examining. This successful photograph extends from about *h* to near D, and shows the remarkable doubling of many of the bright lines by dark ones, a feature which was at once noticed by Father Sidgreaves and ourselves.

In our photograph, the spectrum of the star, which extends on the plate as far into the ultra-violet as our photographs of Sirius, is crowded throughout its entire length with dark and bright lines. In the visible region the number of bright lines and groups, including the double line of sodium, a fine line about the position of $\frac{D}{3}$, and lines on both sides of C, is also very great.

We prefer in this preliminary note not to enter into any more detailed discussion of the star's spectrum, nor to refer to the probable phenomena which may now be in progress in this celestial body. We reserve these considerations for the present.

* A Paper presented to the Royal Society, February 24, 1892

PROFESSOR BUNSEN AND THE CHEMICAL SOCIETY.

It was announced at the last meeting of the Chemical Society that it was proposed to present the following address to Professor Bunsen, who has now been fifty years a Foreign Member of the Society, and the wish was expressed that among those who sign it all those who have been his pupils should, as far as possible, be included. Fellows of the Society who have been pupils of Professor Bunsen are requested to communicate with the Senior Secretary before March 19, in order that they may receive a form for signature.

To Privy Councillor Professor Bunsen, Fellow of the Royal Society.

Your Excellency,

Fifty years have elapsed since the Chemical Society of London honoured itself by electing you one of its Foreign Members. Your name, and that of your illustrious fellow-countryman Liebig, are, in fact, the first on a list which includes the most distinguished cultivators of chemical science in every civilised country of the world.

Our Society remembers with gratitude that you enriched the first volume of its Transactions by communicating to it the results of your ever-memorable investigation of Cacodyl and its Compounds. That you should have sent to us, in the first and most critical year of our existence, a memoir which the chemical world will ever regard as one of the classics of our science, is a significant proof of the beneficent interest with which you regarded our efforts to foster the growth of chemical learning in this country.

Your masterly investigations, in collaboration with our Fellow Sir Lyon Playfair, on the gases evolved from iron furnaces, made by methods which you were the first to bring to perfection, greatly extended our knowledge of the theory of the smelting of iron. By the permanent benefit thus conferred on one of the most important of our industries, you have largely augmented our national wealth.

The half century during which you have been associated with our Society has been fruitful in great discoveries and important inventions. It has witnessed the birth of new elements, the creation of new analytical methods, and an extraordinary development in the instrumental resources of our laboratories. Chemists will never forget that it is to your unwearied assiduity and single-minded devotion that science owes some of the most momentous of these discoveries, and some of the most valuable of these inventions. Your investigations will ever be regarded as models of the highest type of scientific research, and the memoirs in which you have embodied them shed an imperishable lustre on our literature. Your methods of analysis are among the most common of our manipulative operations, and the very furniture and instruments of our laboratories are an ever-present testimony to the obligations under which experimental chemistry will always remain to you.

Many of our members are proud to be numbered among your pupils, and those among them who have become teachers have, we trust, caught and transmitted something, not only of the method, but also of the spirit, in which they themselves were taught. They have an abiding memory of your kindliness, of your constant and unselfish devotion to their interests, and of the generous sympathy and ready help which you extended to their efforts to enlarge the boundaries of our science.

We, the undersigned Fellows of the Chemical Society of London, now beg to offer you our heartfelt felicitations on the occasion of your Jubilee as a member of our body. It is our fervent hope that you may be able, for many years to come, to enjoy the health and happiness the leisure and repose which you have so justly and so honourably earned.

NOTE ON THE MIGRATION OF SALTS.

By Dr. T. L. PHIPSON, F.C.S.,
Graduate of the Faculties of Science and Medicine of the University of Brussels, Member of the Chemical Society of Paris, &c.

DURING the many years that I have devoted to laboratory work, numerous more or less curious instances of the migration of salts have come under my notice. One of the most curious, and at the same time the most beautiful, was obtained by the spontaneous evaporation of a solution of *sulphonaphthalate of ammonia* placed in a very large glass capsule. The crystals formed along the sides of the capsule *over the mother-liquid*, producing the most exquisite representation of a coppice on the borders of a lake. For some weeks it was a cause of admiration and wonder to all who saw it.

But a still more extraordinary case of migration occurred a few years ago, which I will now describe. In 1883, when I published in the CHEM. NEWS a note on the "Constant Production of Oxygen Gas by means of the *Protococcus Pluvialis*," I had a small bottle of pure caustic soda used in analysing the air during these experiments. One morning the stopper was found to be tightly fixed in this bottle, and on striking it rather too impetuously with a knife, I produced three fine cracks, the stopper remaining as firmly fixed as before. The bottle was then put aside on a shelf, and not touched again till five years later. In 1888 it was found that almost the whole of the caustic soda had made its way out of the bottle through these three fine cracks in the upper part of the glass, and appeared on the outside in the form of a bulky covering of effloresced carbonate of soda, a large portion of which had fallen upon the shelf.

In the inside of the bottle are small quantities of minute, moist, quadrangular crystals. It is evident that the hydrate of soda has crawled up under the influence of the moisture of the atmosphere sucked in through the cracks, and has migrated through them to the outside, where, meeting with an ample supply of carbonic acid, it has been converted into carbonate, and this has subsequently effloresced, forming a bulky white covering like snow, a portion of which has fallen around.

In apparent defiance of the laws of gravitation, the contents of this bottle, which has remained in a perfectly quiescent state for five years, have found their way outside through these fine cracks which, occur only in the upper portion of it. It is doubtless a case of *capillarity*, and it may be stated, I think, as a general law that all cases of migration must be looked upon as phenomena of capillarity, although the exact nature of these phenomena seems still to be enveloped in mystery. Instead, however, of looking upon them as exceptions to the laws of gravitation, they must be connected with atmospheric pressure, and so come under their influence.

Laboratory of Analytical Chemistry,
Putney, London, S.W.

A GENERAL LAW APPLICABLE TO GASES AND LIQUIDS.

By J. ALFRED WANKLYN.

ONE of the results flowing from the work upon which I have been engaged for many years, sometimes alone and sometimes in company with my colleagues Cooper and Johnstone, is the unfolding of a great generalisation, applicable alike to gases and liquids, which may be formulated in the following terms:—

Heterogeneity is without influence upon volume, or the volume of a mixture is equal to the sum of the volumes of its constituents separately measured.

Gases.—So far as I am aware—although the reasoning on the simplest examples of gas-analysis involves the admission of the truth of this generalisation as applied to gases—the generalisation has never been explicitly set out. It is not by any means manifest *à priori*, but is founded upon very wide observation.

Thirty-one years ago it fell to my lot to place on record in the *Trans.* of the Royal Society of Edinburgh, a series of observations illustrative of the great truth that gaseous mixtures occupy exactly the same volume as the constituents of the mixture.

The paper has been frequently quoted, because in that paper Sir Lyon Playfair and myself announced the discovery of the duplicate nature of nitric peroxide, which is N_2O_4 at low temperatures and NO_2 at high temperatures. The completeness and the striking character of the evidence bearing upon the fundamental nature of gaseous mixtures has, however, escaped attention altogether, and it will not be out of place to refer to it in a detailed manner. The paper bore the title "On a Mode of Taking the Density of Vapour of Volatile Liquids at Temperatures below the Boiling-Point," by Dr. Lyon Playfair, C.B., F.R.S., and J. A. Wanklyn, F.R.S.E., and it was read January 7, 1861.

The method consisted in measuring the volume occupied by a mixture of a measured quantity of a permanent gas and an ascertained weight of the vapour under investigation; and our paper contained a detailed proof that such mixtures have the same volume as the sum of their constituent volumes, measured separately. We proved this for mixtures of alcohol and hydrogen, for mixtures of ether and hydrogen, for mixtures of nitrate of ethyl and nitrogen, for mixtures of nitric acid and air, and lastly, for the extreme case of a mixture of gaseous ammonia and gaseous water.

This last case I consider to be most important and most decisive. The details are, "a quantity of dry ammonia was measured over mercury, then a small portion of water, which had been accurately weighed in a thin glass bulb, was introduced into the ammonia. The whole was then heated up to 100° C., and the volume of mixed gas and aqueous vapour noted.

	Observed c.c.	T.°	P. m.m.	Corrected vol. at 0·6 and 760 m.m.
NH_3.	39·19	12·5	558·08	24·008
NH_3+H_2O ..	107·32	102	709·66	72·973

The weight of water employed was 0·0402 grm. On calculation it will be found that 0·0402 grm. H_2O yields 49·95 c.c. at 0·6 and 760 m.m., whilst the experiment gave 48·965 c.c., which, bearing in mind the experimental difficulties of such an experiment, is a sufficiently close agreement. In short, there is the most varied evidence that, so long as there is no actual chemical action between the molecules by a gaseous mixture, the fact of the molecules being dissimilar has no influence upon the volume."

Liquids.—The law holds in the instance of liquids just as in the instance of gases. Such, I believe, is the fair interpretation of the results which have been recently published in the CHEMICAL NEWS and in the *Philosophical Magazine*.

In July last Cooper and myself published the preliminary result that a strong solution of cane sugar occupies the same volume as the solid sugar and water of which it is composed, and set down 0·371 as the value of i the increment co-efficient of cane-sugar.

In the November number of the *Phil. Mag.*, an elaborate investigation is published. Employing a half-litre specific gravity bottle, and taking great precautions, and covering a wide range, viz., from 1·3 grms. up to 104·6 grms. of sugar in a litre of solution, we obtain a slightly higher value, viz. :—

Strength, *i e.*, No. of Grms. of Sugar in Litre of Solution.	Sp. gr.	i.
1·341	1000·52	0·3878
9·878	1003·84	0·3887
104·580	1040·60	0·3882

Over this wide range it would seem that i is absolutely constant. When the strength is greatly increased, at 749·5 grms. per litre, for instance, i has been found 0·3762. Such a solution is quite viscid, and the slight depression in the value of i is no doubt due to the departure from perfect fluidity.

The account which we give of the solution of cane-sugar in water is as follows :—

Up to, and no doubt considerably beyond, a strength of 105 grms. sugar in the litre, these sugar solutions are mixtures of fluid sugar (specific gravity 1·634) and water; and they have exactly the same volume as the water and sugar, measured separately. Very strong and viscid solutions—which, in truth, are not quite perfect solutions—exhibit a very slight departure from absolute uniformity. They are mixtures in which the density of the sugar is a little lower, viz., 1·606, which has been recognised as the density of solid sugar. On calculation it comes to this, that in passing from the liquid to the solid state there is a slight expansion, viz., about one-fiftieth. In the viscid solution we find the slightly expanded sugar; but in the dilute and more fluid solutions the fluid sugar is found with its density 1·634.

There is similarity and dissimilarity between saline solutions and solution of sugar. Similarity, inasmuch as i is fairly constant over a great range of strengths in both cases; dissimilarity, since—whilst sugar solutions exhibit no marked contraction—saline solutions show a very decided contraction. In the sugar case $i-i,=0$, but in the saline case $i-i,=C$; and C has a considerable magnitude.

The view which we take of saline solutions is that they are mixtures of fluid hydrates with water, and that the fluid hydrate simply diffuses into the water, or mixes with the water, without change of volume of any kind.

RELATIONS BETWEEN THE ATOMIC WEIGHTS.

By HENRY ADKINS.

THE whole of the atomic weights can be formed from the first four elements :—7 Li, 9 G, 11 B, 12 C. They are formed in a regular sequence by taking a basic number which is either an alkali or an an alkaline earth and adding a regular sequence of the atomic weights; a small anomalous group is the only exception, together with a duplication of 12 in magnesium.

Basic number	7	7	7	7	Alkali	12
Sequence ..	7	9	11	12		12
	14N	16O	(18)?	19F	24Mg	24Mg
Basic number	9	9	9	9	Earth.	
Continued sequence..	14	16	18	19		
	23Na	(25)?	27Al	28Si		

The sequence here is—

7 9 11 12 14 16 18 19

Anomalous Group Alternate Alkali and Earth Base.

Basic numbers	24	23	24	24	24	23	24
Sequence ..	7	9	11	12	14	16	19
	31P	32S	35Cl	36Cl	(38)	39K	(43)?

In this anomalous group it should be noticed that 24 Mg, though higher in atomic weight than 23 Na, yet is made up of two elements only, 12+12=24 Mg, whereas sodium is composed of three elements, 7+9+7=23 Na. This may account for its anomalous position. The atomic weight of Cl, 35·5, seems also to point to its compound character, and is therefore bracketted—

$$\overbrace{35-36}=\frac{71}{2}=35{\cdot}5.$$

The next group continues the sequence from 19 F, but changes the base to 16=7 Li alkali + 9 earth = 16 O.

Basic number	16	16	16	16	16	16	16	16
Sequence	23	24	27	28	31	32	35	36
	39K	40Ca	(43)?	44Sc	(47)?	48Ti	51V	52Cr
Basic number		16		16	16		16	
Sequence ..		39		40	43		44	
		55Mn		56Fe	59N		60Co	

The progressive numbers are—

7 9 11 12 14 16 19 23 24 27 28 31 32 35 36 39 40 43 44,

or from lithium to scandium.

The next basic number is composed of 40 Ca earth; 7 alkali 9 earth = 16, or 40+16=56.

Basic number.

56	56	56	56	56	56	56	56	—	56

Progressive number.

7	9	11	12	14	16	19	23	—	24
63Cu	65Zn	(67)?	(68)	70Ga	72Ge	75As	79Se		80Br

Sequence from 7 to 24.

The next basic number is 39 potassium × 2 = 78, or alkali + alkali.

Basic number	78	78	78	78	78	78	78	78
	7	9	11	12	14	16	(18)	19
	85Rb	87Ir	89Y	90Zr	(92)?	94Nb	96Mo	(97)?

Sequence from 7 to 19. The 18 here is 11+7 of the first group.

The next group takes for its basic number 94, which is 39 K×2=78+7+9=16, or 78+16=94.

Basic number.

94	94	94	94	94	94	94	94

Sequence.

7	9	11	12	14	16	18	19
(101?)	103Ru	105Rh	106Pd	108Ag	(110?)	112Cd	113In

Basic number.

94	94	94	94	94	94	94	94

Sequence.

23	24	27	28	31	32
(117)	118In	(121?)	122Sb	125Te	

The remaining groups are so incomplete that it is difficult to follow farther on this system, but they can be developed in another way.

The basic numbers are 7—9; 7+9=16; 40=7+9=56; 39+39=78; and 39+39+16=94. And the anomalous group 12+12=24; 7+9+7=23.

ON SOME NEW PRODUCTS FROM INDIGO-BLUE.*

By CHARLES O'NEILL.

When a very pure quality of indigo blue (such as is obtained by precipitation from an indigo vat) is treated in a mortar with twenty or thirty times its weight of monohydrated or glacial acetic acid, and permanganate of potash crystals added at intervals with constant stirring and grinding, the blue loses colour, the mass thickens, and upon being examined by a pretty high power of the microscope is found to consist wholly of small prismatic crystals floating in a nearly colourless liquid. Being collected on a filter, washed, and dried in a vacuum, or in air at a temperature of 20°—25° C., the new substance shows as a greyish, greenish, or bluish mass partially matted by the interlacing of the crystals.

Other oxidising matters effect the same change; such are dioxide of lead, red lead,—either added in powder or previously dissolved in glacial acetic acid,—and also the higher oxides of manganese.

The new substance is, no doubt, of a very pale yellow colour, the blue or green tinge being due to a small amount of indigo-blue enclosed in the crystals, which cannot be removed without danger of affecting the integrity of the body itself. The amount of permanganate required is about one-fourth of the weight of the indigo-blue, and equal to yielding one atom of oxygen to one molecule of indigo-blue; a corresponding amount of the other oxidising agents is found sufficient.

The equation representing the change may be expressed as follows:—

$$C_{16}H_{10}N_2O_2+O+2(C_2H_4O_2)=H_2O+C_{20}H_{16}N_2O_6,$$

that is, indigo-blue plus oxygen plus acetic acid yield this body. The constitution of the body not being known it may be provisionally called *oxy-aceto-indigotin*. The calculated yield is about 145 for 100 of indigo-blue; up to 140 per cent has been obtained.

The oxy-aceto-indigotin is insoluble in all solvents which have been tried upon it, it is permanent in dry air, resists decomposition by most neutral, acid, and oxidising agents in the cold, is easily acted upon by alkalies, and is decomposed by heat in any menstrua.

The decompositions of this new body are numerous, and some very complex; attention is for the present directed to only a few cases which are tolerably simple and easily followed. To trace these decompositions the following structure is assumed for the oxy-aceto-indigotin:—

$$C_{20}H_{16}N_2O_6=\left.\begin{matrix}C_8H_5NO\\C_8H_5NO\end{matrix}\right\}O\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O.$$

It is not pretended that this is a true or even a rational arrangement, but it serves as a working hypothesis to explain some changes which the body undergoes.

Decomposition by Heat in Presence of Moisture.

When the oxy-aceto-indigotin is exposed to steam in a shallow vessel or boiled sufficiently long with water, it splits up into indigo-blue, isatin, and acetic acid, the elements of water being added as probably—

$$\left.\begin{matrix}C_8H_5NO\\C_8H_5NO\end{matrix}\right\}O\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}+H_2O=\begin{cases}\text{Indigo, } C_8H_5NO.\\\text{Isatin, } C_8H_5NO_2.\\\text{Acetic acid, } 2(C_2H_4O_2).\end{cases}$$

The calculated yield is acetic acid 31·6 per cent, isatin 34·5 per cent, and indigo-blue 38·7 per cent, which quantities have been frequently obtained. There is, however, usually a fourth body found in variable amounts from 1 per cent to 10 per cent which is less soluble in water than isatin, is dissolved by carbon disulphide in which isatin is insoluble, and crystallises from chloroform in silky golden-yellow crystals. It is believed to be formed by the interaction of indigo and isatin at the moment of their formation (*in statu nascendi*), and to be an oxidised product intermediate between these two bodies. A similar substance is produced under certain conditions by the direct oxidation of indigo-blue.

Decomposition by Dry Heat.

It requires a temperature of about 180° C. to completely decompose the oxy-aceto-indigotin, it loses 31—32 per cent in weight, and yields as distillate mono-hydrated acetic acid readily crystallisable; the residuum in the retort consists of indigo-blue and a red resinous matter which is best dissolved from the indigo by chloroform, leaving pure indigo; no isatin is produced.

Decomposition with Sodium Hydrate.

If the oxy-aceto-indigotin be mixed with solution of sodium hydrate in the cold, it speedily becomes blue-coloured, and in the course of some time may be filtered; indigo-blue is left on the filter, and a slightly yellowish filtrate is obtained; upon the addition of a mineral acid to the filtrate a precipitate is produced which, when separated, proves to be a new acid body which may, perhaps, properly be called *indigotic acid*. Using the scheme of construction given above, the decomposition may be assumed as follows:—

$$\left.\begin{matrix}C_8H_5NO\\C_8H_5NO\end{matrix}\right\}O\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O+3NaOH=$$

$$=\begin{cases}\text{Indigo-blue, } C_8H_5NO.\\\text{Indigotic acid, } C_8H_7NO_3.\\\text{Acetic acid, } 2(C_2H_4O_2).\end{cases}$$

The Na of the sodium hydrate is replaced in this equation by H for sake of clearness and simplicity. The hypothetical acid $C_8H_7NO_3$ would be truly isatic acid, or isatin with the elements of water added; but upon combining the acid with bases it is found that the above formula must be quadrupled and stands $C_{32}H_{28}N_4O_{12}$.

This indigotic acid is yellowish or brownish in the crude state, but can be bleached by animal charcoal, and forms small brilliant crystals very soluble in alcohol, sufficiently soluble in hot water to obtain it in a good crystalline state, requires about 1000 parts of cold water for solution, and has a strongly acid reaction to litmus. It is decomposed at about 240° C., appears to fuse, but gives off vapours, among which aniline can be detected. It is polybasic, and forms at least two series of salts: the neutral sodium salt $C_{32}H_{26}Na_2N_4O_{12}$ is very soluble and not crystallisable; the acid salt $C_{32}H_{27}NaN_4O_{12}$ is less soluble and crystallises well from water.

Decomposition in Strong Acetic Acid.

When the oxy-aceto-indigotin is heated with glacial acetic acid it is decomposed, yielding indigo-blue and brilliant yellow crystals. The decomposition here appears to be of a strictly intra-molecular character, as—

$$\left.\begin{matrix}C_8H_5NO\\C_8H_5NO\end{matrix}\right\}O\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O=\begin{cases}2(C_2H_4O_2), \text{ acetic acid.}\\C_8H_5NO, \text{ indigo.}\\C_8H_5NO, \text{ new substance.}\end{cases}$$

Analysis justifies the formula of the latter body, which has not been fully examined.

* Abstracted by the author from a communication to the Manchester Literary and Philosophical Society, Feb. 23, 1892.

Enamelled Water-Baths with Ring Supports of Enamel.—B. Fischer (*Zeit. f. Angewandte Chemie*) proposes this material in order, in toxicological investigations, to exclude the possibility of traces of copper being introduced into the objects examined. Brass gas-burners have given rise to the introduction of traces of copper; whence the author proposes iron burners and glass lamps.

IMPROVEMENTS IN BURETTES.

By ALEX. F. REID, of Bonshaw, Stewarton, N.B.

IN a former article (CHEM. NEWS, vlo. lxv., p. 68) I described an apparatus for measuring out liquids which may also be used as a burette. I will now describe an appendage to an ordinary burette which I find very useful when successive small quantities of solution are taken from the same burette. It consists of a sliding scale or vernier of sheet metal which slides on the outside of the burette.

It is shown on an enlarged scale in fig. 1 and on the burette in fig. 2.

FIG I

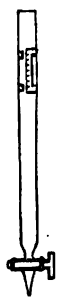

FIG II

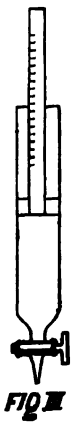

FIG III

An arrangement serving a similar purpose is shown in fig. 3, which consists of a burette of a rather large bore with a graduated tube inside. An india-rubber band is firmly fixed round the bottom of this tube so as to form a piston which slides inside the burette. By shoving down the inside tube after each titration the surface of the liquid is brought to the zero of the scale.

ILLUMINATING FLAMES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S.

Concluded from p. 114).

WITH this arrangement I was able to map out the temperatures existing in the flat flame, in which I had traced out the changes taking place in the constituents of the gas; and I found that the temperature rapidly rose from 500° C. half an inch above the burner, to a little over 1200° C. at the commencement of the luminous zone—the luminous edges having a temperature of 1216° C.; and these temperatures were further increased in the luminous zone until near the top of the flame 1368° C. was reached. This at once gives us the secret of the luminosity. From the mouth of the jet and up to a temperature of 1000° to 1200° C., we have the formation of acetylene from the original hydrocarbons; but the moment the requisite temperature is reached by the combustion of the hydrogen and the carbon monoxide, the acetylene decomposes, with a further rise of temperature, and the carbon heated to incandescence radiates heat and light.

If a luminous flame be cooled, its luminosity is at once diminished, and may be destroyed; while, as the propagation of flame requires a certain temperature, a further cooling will extinguish it. In the outer edge of a flame, the rapid inrush of air sucked into the flame so lowers the temperature that a thin envelope is rendered non-luminous, the actions checked, and traces of the gas allowed to escape unconsumed by the extinction of the extreme limit of the flame; and delicate analysis shows that every luminous flame burning freely in air gives off distinct traces of carbon monoxide, acetylene, and even such highly-inflammable gases as methane and hydrogen.

Ever since the structure of flame has been noted and discussed, it has been accepted as a fact beyond dispute that the outer almost invisible zone which is interposed between the air and the luminous zone of the flame is the area of complete combustion, and that here the unburnt remnants of the flame gases, meeting the air, freely take up oxygen, and are converted into the comparatively harmless products of combustion, carbon dioxide, and water vapour, which only need partial removal by any hap-hazard process of ventilation to keep the air of a room fit to support animal life. The facts I have brought before you show that this is not the case; and they fully explain why gas is so oppressive in a badly-ventilated apartment.

It has always been the custom to speak of flame as built up of zones; and although there are no sharp lines of demarcation in the actions taking place which would warrant this, still three distinct portions are visible to the eye. If we divide the luminous flame into zones, it would be perhaps best looked upon as consisting of three, viz.:—

1. The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to about 1000° C. at the apex of the zone. In this portion of the flame the constituents of the gas undergo various decompositions and interactions, which culminate in the conversion of the heavier hydrocarbons into acetylene—carbon monoxide being also produced; and these, with the products of combustion and residual hydrogen, pass into the next phase of action.
2. The luminous zone, in which the temperature ranges from 1000° C. up to a little over 1300° C. Here the acetylene formed in the inner zone becomes decomposed by heat, with liberation of carbon, which, at the moment of production, is heated to incandescence by the combustion of the carbon monoxide and hydrogen, and gives luminosity to the flame.
3. The extreme outer zone, in which, combustion being nearly completed, the cooling and diluting influence of the entering air renders a thin layer of the flame non-luminous, and finally extinguishes it. With ordinary coal gas, this results in the escape of traces of hydrogen, methane, carbon monoxide, and acetylene; while with a very rich gas unconsumed carbon also escapes.

This description of a luminous flame is of necessity far from complete, as it leaves out of consideration the interactions which lead to the formation of acetylene, and also the decompositions going on in the various parts of the flame between the products of combustion and the flame gases; but I think it marks a considerable advance in our knowlege of the main actions which lead to luminosity—the other interactions being at best subsidiary to it.

Having obtained a clear idea of the causes which lead to luminosity in flame, we are enabled for the first time to clearly understand the actions taking place in the atmospheric or Bunsen burner, the invention of which revolutionised our methods of heating by gas, and made coal gas one of the most important of our domestic fuels.

When it was first found that the admixture of a certain proportion of air with coal gas before combustion caused it to burn with a non-luminous flame, it was at once accepted, as an explanation of the phenomenon, that the extra oxygen so led into the inner cone of the flame, by causing complete combustion in the central zone, burnt up the carbon before it could be heated to incandescence, and so destroyed its light-giving power. Some years later,

* A Lecture delivered at the London Institution, February 18th.—From the *Journal o Gas Lighting*.

however, Knapp and others showed that, by mingling inert diluents, such as nitrogen, carbon dioxide, or even steam, with the gas before combustion, non-luminosity could be produced. It was then recognised that the diluting and cooling action of the nitrogen in air played an important part; and some observers held that it was this, and not the oxygen, which was the cause of non-luminosity.

On measuring the amount of air and of nitrogen respectively able to render a Bunsen flame non-luminous, they are found to be practically the same, while the quantity of oxygen present in the air used, when passed into the gas by itself, still gives a very luminous flame. This certainly looks as if it were the nitrogen that was doing the work. If this were so, the temperature of the flame rendered non-luminous by nitrogen should be the same as that of the flame rendered non-luminous by air; but, on testing these, the fallacy of such a supposition is at once exposed. This will be seen by the following table:—

Part of flame.	Temperatures existing in a Bunsen flame rendered non-luminous by— Nitrogen.	Air.
½ inch above burner ..	30° C.	54° C.
1½ inches above burner ..	111°	175°
Tip of inner cone	444°	1090°
Centre of inner cone ..	999°	1533°
Tip of outer cone	1151°	1175°

These temperatures clearly show that a very considerable amount of combustion is due to the oxygen of the air, and make it perfectly manifest that both the oxygen and the nitrogen are acting in bringing about the loss of luminosity.

While working at these points, I found that if mixtures of nitrogen and oxygen, poorer in oxygen than air, were employed, it was practically only the nitrogen which acted—the diluting effect being so strong that the oxygen was prevented from taking any active part. With air, both act; while with mixtures richer in oxygen than air, the oxygen alone acts—the nitrogen being apparently unable to exercise any retarding influence. The same result is obtained if excess of air is mixed with the gas before combustion. If the quantity of air reaches a point at which the proportion of oxygen in the air is to the gas as 0·5 : 1, then the diluting influence of the nitrogen is lost, and the appearance of the flame becomes entirely altered. The normal Bunsen flame burns with a lilac-coloured inner and blue outer zone; but the moment the quantity of air admitted reaches the ratio mentioned, the flame becomes short and fierce, and the inner zone changes to a greenish colour,—the highest temperature in the flame at the same time increasing by nearly 100° C. Experiments show that the nitrogen acts in the normal Bunsen flame by so diluting and protecting the hydrocarbons that a far higher temperature is needed for their decomposition; and this action gives time for the oxygen of the air to consume them without liberation of carbon, and hence without luminosity.

In conclusion, I think that we may express the actions which lead to the loss of luminosity in the normal Bunsen flame in the following way:—

1. The chemical activity of the oxygen introduced in the air, which, by burning up the molecules of hydrocarbons before, in their diluted condition, they undergo decomposition, causes loss of luminosity.
2. The diluting action of the nitrogen of the air, which, by increasing the temperature necessary to bring about the partial decomposition of the hydrocarbons, prevents formation of acetylene, and in this way will, by itself, cause non-luminosity; and in the normal Bunsen flame it acts by doing this until destruction of the hydrocarbons by oxidation has taken place.
3. The cooling influence of the air introduced, which is able to add to the general result, although the cooling is less than the increase in temperature brought about by the oxidation due to the oxygen in the air.

ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.*

By WALTER MAXWELL.

These investigations have been conducted with the purpose of acquiring some further data showing the comparative proportions of matters which become separated from vegetable organisms by extracting with pure ether in variable durations of time. It has further been attempted to determine whether the whole of the substituted glycerides, or lecithines, do become separated by direct extraction with ether only.

The materials used in the work were pulverised to the greatest state of fineness, and the extractions were made with the Knorr extraction apparatus. The calculations are reduced to the standard of water-free material.

(*a*) The preliminary experiments, which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time, are illustrated by the following results:—

Cotton-Seed.

Time. Hours.	Weight of material. Grms.	Weight of extract. Grms.	Per cent.
8½	4	1·472	37·39
10	4	1·491	37·87
15	4	1·511	38·38

These results give the average of a great number of analyses. Although an increased amount of substance becomes separated with an increased duration of the period of extraction, the proportion is small; and it is not apparent that the greater duration of time causes an increase in the fatty bodies only, as other matters can be affected by a very protracted boiling. For these reasons it has been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether in a duration of fifteen hours.

In considering the estimation of the proportions of glycerides and substituted glycerides which are contained in the ether extract, the presence of other bodies, which have been removed with the ether, make it impossible, in the absence of an absolute analysis of the extract, to determine accurately the comparative relations of those fatty bodies. The ether extractions of plant matters contain variable proportions of cholesterin and of, in some instances, solid hydrocarbons, which may constitute several per cent of the extract. However, although the percentage of glycerides cannot be definitely estimated, the lecithines or substituted glycerides may be determined with absolute accuracy, as the estimation of these bodies rests upon the proportion of phosphorus present in the ether extract. The extract is combusted with mixed alkali salts, by which the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate, and is then determined as magnesium pyrophosphate, and the latter body being multiplied with the known Hoppe-Seyler factor, gives the exact amount of lecithine.

A further series of extractions was made of the pulverised cotton-seed with pure ether for a period of fifteen hours, and the total extract determined. The proportion of lecithine contained in the extract was estimated by the method already given, the residue of the extract being

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

considered as glycerides and other bodies. The average of eight analyses gave the following results:—

Extract..	38·46 per cent.
Glycerides, &c.	98·84 ,,
Lecithines	1·16 ,,

(*b*) It will be shown that the proportion of substituted glycerides stated, 1·16 per cent, does not represent the total lecithine present in the cotton-seed.

The observation was made simultaneously by Prof. E. Shulze, Zurich, and W. Maxwell, Harvard College, that the substituted glycerides do not become wholly separated by extraction with ether, even in a great duration of time. It was found that if the material which had been already extracted with ether were further extracted with absolute alcohol another portion of substituted glycerides was obtained, which in most instances was greater than the amount separated by the ether. The process of the alcohol extraction consisted in merely extracting the material already treated with ether, and evaporating off the alcohol and re-extracting the alcohol extract residue with ether. The reason for taking up the lecithines out of the alcohol extract was that it has been observed that those lecithines which were originally insoluble in ether became soluble in that menstruum when previously acted upon by alcohol. The use of ether was further made in order to avoid any small portion of inorganic phosphates which might have been removed from the vegetable material by alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol.

The amount of the ether extraction of the alcohol extract in one hundred parts of the vegetable material with the proportion of lecithines was as follows:—

Extract	2·3 per cent.
Lecithines in extract	16·6 ,,

A further comparison indicates the following:—

	Extract. Per cent.	Lecithines. Per cent.	Glycerides, &c. Per cent.
Ether	38·46	1·16	98·84
Ether and alcohol.	40·76	2·30	97·69

The proportion of lecithines to the total fatty bodies contained in the cotton-seed is very small, yet it is seen that about 50 per cent of those substituted glycerides are left in the material after extraction with ether for a period of fifteen hours. If certain other varieties of seeds be considered, such as the legumes, pea, vetch, bean, Boston bean, &c., it is found that the total ether and alcohol extracts of those seeds are composed of lecithines varying from 25 to 45 per cent. It is thus apparent that in the examples of seeds given as far as 20 per cent to 25 per cent of the total fatty bodies can remain unseparated and undetermined when the material is extracted with ether only.

THE BEHAVIOUR OF BARIUM PEROXIDE WITH METALLIC SALTS.

By H. KWASNIK.

In 1890 the first assistant at the Pharmaceutical Institute at Breslau, Dr. Kassner, published two methods for the volumetrical determination of potassium ferricyanide and the peroxides of the alkaline earths, using for the former the reaction of hydrogen peroxide and potassium ferricyanide, and for the latter that of barium peroxide and potassium ferricyanide. This latter reaction took an unexpected form, since the total oxygen is liberated as such without the formation of ozone or hydrogen peroxide, but with a reduction of the ferricyanide according to the equation—

$$BaO_2 + Fe_2Cy_{12}K_6 = O_2 + K_6Ba(FeCy_6)_2.$$

(VI)

The process takes place so definitely that it is sufficient to cover equivalent quantities of barium peroxide and potassium ferricyanide with cold water in order to obtain at once a copious evolution of pure oxygen. Why obtain from 2·3 grms. of barium peroxide at 75 per cent about 240 c.c. of oxygen, whilst theory requires 236 c.c. ?

In connection with this I made the observation that ferric chloride with barium peroxide likewise produces a copious liberation of oxygen, but here there ensues no reduction of the ferric salt, and consequently only half the oxygen of the barium peroxide is liberated, according to the equation—

$$6BaO_2 + 2Fe_2Cl_6 + 6H_2O = 3O_2 = 2Fe_2(OH)_6 + 6BaCl_2.$$

At the instigation of Herr Poleck I have pursued this subject further, and have studied the action of a great number of metallic salts upon barium peroxide, whereby I have arrived at results which were novel and not devoid of interest.

On repeating the experiment above described, that only the half of the oxygen of the barium peroxide is given off, no trace of a ferrous salt is formed, nor is there any formation of hydrogen peroxide or of ozone. It was further found that all the ferric salts, sulphates, nitrates, acetates, &c., act in the same manner, and that the behaviour of the ferrous salts is similar, though more tedious, since the escaping oxygen first peroxidises the ferrous compound, after which ensues the liberation of oxygen, in this case only to the extent of one-fourth part, according to the equation—

$$4FeCl_2 + 4BaO_2 + 6H_2O = Fe_2(OH)_6 + BaCl_2 + O_2.$$

As for the action of metallic salts in general upon barium peroxide, the salts of potassium, sodium, lithium, ammonium, calcium, strontium, and barium have no action, not the slightest escape of gas occurring even on the application of a gentle heat. Heating up to 100° must be avoided, since under such circumstances barium peroxide alone evolves oxygen.

The magnesium salts react, but the development of gas begins only after some time, whilst salts of zinc and cadmium react more rapidly, and salts of cobalt and nickel produce immediately a strong liberation of oxygen. In the latter case the mixture takes the colour of the hydroxide concerned. Salts of manganese, chromium, and aluminium behave similarly to ferric chloride; salts of copper effect an abundant escape of oxygen without reduction; whilst the above mentioned salts liberate half the oxygen combined with the barium, with a simultaneous formation of hydroxides, the group of noble metals have a decidedly different behaviour.

Mercury salts experience at once a decided reduction with barium peroxide. Oxygen is given off, and the mixture becomes constantly darker; metallic mercury is separated as a blackish grey powder, which, on treatment with dilute hydrochloric acid, sometimes coalesces into metallic globules, $HgCl_2 + BaO_2 = BaCl_2 + Hg + O_2$.

The behaviour of the silver salts is quite similar. They yield a black-grey deposit with a copious evolution of oxygen. The precipitate dissolves in ammonia only to a very slight extent, occasioned by small quantities of barium oxide; after removal of the excess of barium peroxide by treatment with dilute hydrochloric acid metallic silver remains behind as a grey powder.

In a similar manner metallic gold is separated from gold salts as a brown-black powder. In very dilute solutions of gold, and if the reaction is caused to be as slow as possible, the same phenomena are observed as on the reduction of gold salts by oxalic acid. The liquid first takes a blue tone, and after some time the gold is deposited upon the sides of the vessel as a brilliant mirror.

Whilst these reactions take place definitely platinum chloride shows a different behaviour. It is not reduced to metal, although there is here an escape of oxygen. The liquid remains yellow even on the addition of a large excess of barium peroxide,—a result which is not modified by heat. The filtrate was evaporated down on the water

bath and precipitated with absolute alcohol. The light, orange-coloured precipitate was washed with alcohol, then dissolved in water and re-crystallised by evaporation. The crystals were $PtCl_4BaCl_2+8H_2O$. The platinum found was 28·24 per cent, whilst theory required 28·73 per cent. In these experiments the ordinary platinum chloride solution of laboratories was used containing $PtCl_42HCl$, which easily explains the formation of the double compound—

$$2PtCl_42HCl+2BaO_2=2PtCl_4BaCl_2+2H_2O+O_2.$$

It is perfectly indifferent in its behaviour with platinum peroxide; the behaviour of the other platinum double salts of alkalies and alkaline earths was identical, no platinum being reduced from any of them. But the action of barium peroxide is quite different upon pure platinum chloride, and upon its double compounds with the salts of metals which disengage oxygen from barium peroxide. If a molecule of the compound $PtCl_42HCl$ is mixed in an aqueous solution of two molecules silver nitrate, there separates out a mixture of platinum chloride and silver chloride, $PtCl_42AgCl$, and of silver chloride, whilst there is formed at the same time a reddish-yellow solution of platinum chloride free from silver. If this mixture is exposed to the action of barium peroxide, oxygen is given off and black flocks are deposited, whilst if an excess of barium superoxide is added, the supernatant yellow liquid is decolourised, proving the decomposition of the platinum chloride. In fact, after the excess of barium precipitate has been removed by means of dilute hydrochloric acid, the precipitate consists merely of metallic platinum and silver.

The fact that silver chloride, insoluble in water, is reduced by the action of barium peroxide, with the elimination of its entire quantity of oxygen, led to an examination of other insoluble metallic salts. As a result of the examination of insoluble sulphates, carbonates, phosphates, arseniates, it was found that the selection of the acid had no influence upon the course of the reaction; oxygen was given off in every case with a formation of the respective hydroxides, though the action is naturally here slower. Whilst in some of these insoluble salts the reaction must be initiated by the application of heat, in others the process takes place easily, as in ferrous phosphate, copper carbonate, mercurous chloride, and silver chloride. The reduction of silver chloride by this method is easily effected.—*Ber. Deut. Chem. Gesell.*, xxv., p. 67.

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

FOURTH MEETING, 1892, HOBART.

The grand vision of a pan-Britannic Association for the Advancement of Science has melted away in conflict with the stern realities of time and space. Few, indeed, of our African, Indian, not to speak of Australian, colleagues could spare the time for a yearly or even decennial visit to Britain. Even if the gathering were to take place, say, at Cape Town, the inconvenience would be merely transferred, not abrogated.

Such being the case, we must unfeignedly rejoice at the rise and progress of the Australian Association. This itinerant body is founded on the lines of the British Association. Its meetings are held by rotation in each of the Australasian Colonies. It has its sections, its presidential addresses, its meetings for reading and discussing papers, its excursions, its receptions and garden parties, and even its "science sermon." But along with the general features of its forerunner, it has adopted a few of the defects of the latter, and has called into being some undesirable features, from which our old "B A" has been free. The number of sections has been increased. We see under A "Astronomy, Mathematics, Physics, and Mechanics." It is undeniable that not a few astronomical phenomena may be studied to more advantage in Australia than in Europe. But mathematics, physics, and mechanics present no such local facilities. Whatever could be effected in those sciences in Australia might be done quite as well in Britain, France, or Germany.

With section B (chemistry and mineralogy) the case is different. Numbers of Australian plants—and some animals—contain proximate principles which demand and merit thorough investigation. Nor have all the local minerals been fully explored.

In section C (geology and palæontology) the state of affairs is very similar. But the most tempting and, doubtless, the most remunerative field is presented by section D (biology). We must say that here the ground has been merely scratched. As many of the plants and animals are the friends of man, and others his deadly enemies, there are here practical reasons for careful study. Concerning section E (geography) there is still scope for work under the Southern Cross.

Section F (economic and social science, and statistics) has been one of the defects of the British Association. Statistics cannot be regarded as a science, but as a method. Economics slide too easily into party politics, and meet with ample scope in chambers of commerce, municipal bodies, &c. Sociology is not yet constituted as a science. All of us will remember the "social science congresses" in England, which, it was drily said, were gatherings "of men who ought to have been women, and of women who repined that they were not men."

Section G (anthropology) might, perhaps, have been included under D.

For sanitary science and hygiene (H) there is, we fear, too great a need. It is humiliating for the British Empire and the British races, that both in Australia and South Africa we have successfully acclimatised typhoid fever and diphtheria!

Section I (literature and fine art) has been found in England a dangerous neighbour to science. In the so-called Literary and Philosophical Societies of England, *e.g.*, that of Liverpool, science would be benefitted by a process of dissociation. But why, we would ask, is there not a section for agricultural science?

Section J (architecture and engineering) might be usefully divided. Engineering might be combined with section A, and architecture might rank as a fine art under section I.

The projected excursions, especially those to the silver fields and tin mines, and the salmon ponds, promise to be intensely interesting. It is decidedly exceptional to find good silver deposits in the Eastern Hemisphere. The Mount Bischoff Tin Mine asserts a claim to be the largest tin mine in the world. At least, it has turned out upwards of 53,000 tons of tin, employs regularly 380 men and boys, and has the cardinal virtue of paying good dividends.

We have not yet received copies of the Presidential Address and of the papers read before the sections, but some of them, as far as we can judge from the titles, promise to be exceedingly important. We wish the Australasian Association a long and splendid career.

Dispersion of Prism-Spectroscopes.—G. Guglielmo.—The author, in order to increase the dispersion of such spectroscopes, places in front of the lower halves of the object-lenses of the collimator and the observing telescope glass mirrors silvered on their front sides, slightly inclined towards the perpendicular. Thus a part of the light is several times transmitted backwards and forwards through the prism, and the dispersion is considerably increased. A great loss of light is inevitable.—*Rendicon. de la Reale Acc. dei Lincei*, vi., 195.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 26, 1892.

Prof. W. E. AYRTON, F.R.S., Past President, in the Chair.

PROF. S. P. THOMPSON, F.R.S., read a paper "*On Modes of Representing Electromotive Forces and Currents in Diagrams.*"

The author said he had found it advantageous in some cases to depart from the usual methods of representation, and he now brought the subject before the Society in order to have it discussed and improvements suggested.

To indicate the direction of currents in wires seen end-on, Mr. Swinburne had used circles with and without crosses, but no symbol had been suggested for wires not conveying currents. He (Prof. Thompson) thought the plain circle should be used for inactive wires. A circle with a dot in the middle could then be used to indicate that a current was flowing towards the observer, and a circle with a cross in it to represent a wire conveying a current away. These meanings could be recalled by considering the direction indicated by an arrow; the dot showing the tip of the arrow, and the cross the feathers.

Some method of distinguishing between E.M.F. and current was required. For this, he proposed to use thin stemmed arrows with feathers for E.M.F.'s, and thick stemmed ones without tails for currents. In the case of electrical transmission of energy, this convention had the important advantage that where the two arrows had the same direction, energy was being given to the system, and where the arrows were opposite, energy was leaving it.

Mr. Maycock, he said, had recently published a simple rule for finding the direction of magnetic force due to a current of known direction in a wire. Grasp the wire with the right hand, the thumb pointing in the direction of the current; the fingers will then encircle the wire in the direction of the magnetic force. Dr. Fleming's well-known rule for induced currents was also a *right-hand* rule, but as it referred to the direction of *currents*, another rule was necessary when considering motors. By making the rule refer to E.M.F.'s only, one rule was required for generators and motors.

For alternating currents, the author found it convenient to draw polar curves analogous to Zeuner's valve diagrams. Suppose a line, O P (Fig. 1), representing the

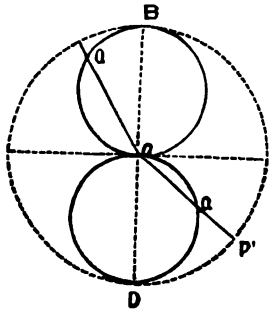

FIG. 1.

maximum value of an E.M.F. or current whose magnitude is a sine function of the time, to revolve at uniform velocity about o; the intercepts, O Q and O Q', &c., cut off by circles, O Q B, O Q' D, will represent the magnitudes at the times corresponding to the positions O P and O P'. The effect of lag can also be represented in such diagrams.

In cases where the variables are not sine functions, the curves O Q B and O Q' D are no longer circles. Polar diagrams, representing the E.M.F. and current curves obtained by Prof. Ryan in his transformer experiments were exhibited, and a working diagram illustrating the changes in three phase currents was shown.

To show the directions of induced E.M.F.'s in diagrams of dynamos and motors, diagonal shading of the pole faces was sometimes convenient; the lines over north poles being drawn from left to right downwards in in the direction of the middle stroke of the letter N, and those over south poles from left to right upwards. A conductor passing over a north pole from left to right would have an E.M.F. induced in a downward direction, as indicated by the slope of the diagonal lines. This method of representation was used to show the ways of connecting up multipolar drum armatures, the winding being supposed cut along a generating line, unwrapped from the core, and laid out flat in the manner adopted by Fritsche.

In connection with armatures, the author said a formula had been published by means of which the nature of a winding consisting of a given number of convolutions and to be used with a given number of poles could be predetermined. This, he thought, would be very useful in practice.

Mr. BLAKESLEY said the old method of representing alternate current magnitudes by means of the projections of revolving lines seemed preferable, for it left no ambiguity as to the directions of the quantities. The method of shading the poles also required that the direction in which the diagram was to be viewed should be known before the direction of the E.M.F. could be determined.

Mr. SWINBURNE suggested that the author might use a bow to represent E.M.F., and an arrow for current. He was glad to see that Prof. Thompson recognised the differences in dynamos and motors, and approved of the view that nmemonic rules should refer to E.M.F., and not to current. The diagrams of drum windings would be very useful, and he hoped the author would make the subject clear to ordinary workmen in the next edition of "Dynamo-Electric Machinery."

Prof. PERRY considered it undesirable to use the polar curves for anything but circles. In his opinion, it was not sufficiently known that any curve can be split up into a series of sine curves, and each component dealt with separately, the separate results being added together in the end.

Mr. SWINBURNE pointed out that before one could analyse a curve in this way, the curve must be known, and would probably have to be determined experimentally. If means for finding one curve are available, any other required curve could probably be found by the same apparatus; hence there was no need for analysis.

Prof. PERRY remarked that experiments could not be made on a machine before the machine was built; whereas the E.M.F. curve could be pre-determined from its design. By analysis, its current curves when working under various conditions could be found.

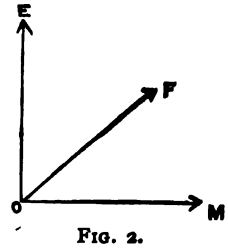

FIG. 2.

Prof. AYRTON, referring to the mnemonic character of the modes of representation described by Dr. Thompson suggested that the symbols in the author's book should

be more mnemonic. He himself was in the habit of using large letters for currents, and small ones for resistances; A and a for the armature, S and s for series, and Z and z for the shunt, currents, and resistances respectively, and σ and ζ for the series and shunt turns. He also found the following "electromotive force" rule very convenient:—Draw three rectangular axes, O M, O F, and O E, as shown in Fig. 2. If then, O F represents the direction of the force (magnetic), O M that of the motion, then O E shows the direction of the induced E.M.F.

Dr. Thompson, in replying, said he thought Mr. Blakesley had misunderstood what had been said, for no ambiguity existed.

In describing the windings of armatures, difficulty arose from want of proper names for the various elements, and in his forthcoming work suitable names had been given. To Prof. Ayrton he pointed out that in his book he (Dr. Thompson) had used mnemonic characters; for r_a, r_s, and r_m, represented the resistances of the armature, shunt, and series magnet coils respectively. The symbol I for current had also been recommended for adoption by the Frankfort Committee. He objected to Greek letters except for specific quantities, such as angles, specific inductive capacities, refractive indices, &c.

He appreciated the simplicity of Prof. Ayrton's E.M.F. rule, but thought it would be better to rotate O E and O F through a right angle about O M, thus giving Fig. 3.

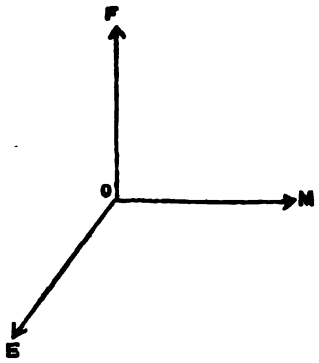

Fig. 3.

A paper on the "*Flexure of Long Pillars under their own Weight*," by Prof. M. Fitzgerald, M.B., was read by Mr. Blakesley. The subject of upright pillars fixed at the base and free at the top is treated mathematically, the differential equation being integrated in two series, involving ascending powers of the variable. Putting L for the ratio of length to diameter, the result, when applied to thin steel tubes and rods, for which Young's Modulus is taken as 12,000 tons per square inch, show that the limiting height (in feet) of pillars which can stand without bending is given by $H=\frac{15\times10^6}{L^2}$ for tubes and $H=\frac{7\cdot5\times10^6}{L^2}$ for rods.

If L = 100 the maximum height of a tube is 1500 feet, the diameter being 15 feet. For wires, L may have larger values, and the limiting length of a No. 28 B.W.A. steel wire is about 10 feet.

In the case of pillars whose neutral axes are constrained to be vertical both at top and bottom the results show that a definite ratio must exist between the bending moments producing the constraint.

A paper on "Choking Coils" by Prof. Perry, F.R.S., and a Description of the Uses of Rice's Choking Coils for Regulating the Brilliancy of Incandescent Lamps, by Mr. Hammer, were postponed until next meeting.

NOTICES OF BOOKS.

A Treatise on Chemistry. By Sir H. E. Roscoe, F.R.S., and C. Schorlemmer, F.R.S. Vol. III. *The Chemistry of the Hydrocarbons and their Derivatives; or, Organic Chemistry.* Part VI. (8vo., pp. 582). London and New York: Macmillan and Co.

The authors of this work are still grappling with their enormous task, the end of which is not yet. The progress of organic chemistry is now so rapid that it is not easily overtaken. The groups of compounds here described are the indene, the naphthalene, the methylnaphthalene, the dimethylnaphthalene, and the ethylnaphthalene groups; then follow the naphthalene derivatives containing more than twelve atoms of carbon; the naphthindole derivatives; acenaphthene group; the pyrene, diphenyl, methyldiphenyl, dimethyldiphenyl, and ethyldiphenyl groups; the derivatives of diphenyl containing more than fourteen atoms of carbon; the azo dyes of the diphenyl group; the fluorine, phenanthrene, retene, fluoranthene, phenylnaphthalene, chrysene, dinaphthyl, diphenylbenzene, and triphenylbenzene groups.

The chief practical interest of a large proportion of the compounds here described depends on their proposed or possible applications in dyeing and tissue-printing. Not, indeed, that all these colouring-matters are in actual use. Many of them have been abandoned on account of some undesirable feature, others because they are too expensive, and others, again, simply because they present no well-marked advantage over their rivals.

Mention is made of the method of producing azo-dyes directly upon the fibre—a process which is ascribed, as we believe correctly, to Holliday. Whether analogous methods will become extended experience must decide.

Among the many curious facts here mentioned, we may refer to the poisonous character of α-hydrojuglone, a compound obtainable from the green shells of the walnut. Even goats are found to perish if they indulge in a raid upon walnut trees.

Many of the naphthalene compounds are mentioned as giving off exceedingly offensive odours. This property is not to be despised, since such compounds may prove exceedingly valuable in repelling those insect parasites with which our crops and even our persons are so persistently beset. We should recommend careful research in this direction.

A very useful feature of the book is that, as in former volumes, the reader is constantly referred in foot-notes to original memoirs, to patent specifications, &c., where the fullest details may be found.

The index is very copious, and, so far as we have been able to test it, remarkably correct.

The work, as a whole, is beyond question the best systematic compendium of chemistry of the age.

Chemical Calculations. With Explanatory Notes, Problems, and Answers. Specially adapted for Use in Colleges and Science Schools. By R. Lloyd Whiteley, F.I.C. With a Preface by Prof. F. Clowes, D.Sc., F.I.C. London: Longmans, Green, and Co. Small 8vo., pp. 100.

It has been confessed that one main reason for the delay in the introduction of the experimental sciences into English schools and universities is the fact that they do not lend themselves readily to the examinational system of education which we have acclimatised from its native China. Works like the present seem, therefore, to have met with the readier acceptance among us because they enable the student to say that he is learning chemistry, whilst at the same time he is doing little to cultivate his powers of observation and of tracing phenomena to their sources.

Mr. Whiteley's treatise, though good of its kind, is

avowedly and intensely examinational. Says Prof. F. Clowes, with subtle irony, "it is safe to predict that it will be found to meet the requirements of candidates for the various university, professional, and Government examinations which now serve as tests of chemical knowledge." How illusive such tests must necessarily prove has been shown over and over again. Suppose two students, one of whom is strikingly successful in answering the questions here given, and the other as signally unsuccessful, we submit that both may still be equally competent or equally unable either to extend the boundaries of the Science or to apply its laws to industrial purposes.

Royal University of Studies at Rome. Chemical Institute. Researches executed in the Scholastic Year 1890—1891. (Regia Universita degli Studi di Roma. Istituto Cnimico. Ricerche esequite nell'ano Scolastico 1890—1891). Rome: Printing Office of the Lyncean Academy.

THIS volume, for which we are indebted to the courtesy of Prof. Cannizzaro, affords satisfactory proof that Italy is not backward in chemical research. Some of the memoirs here contained are exceedingly elaborate, and bring to light very interesting results. We may especially mention a paper by F. Marino-Zuca on a new alkaloid extracted from a species of chrysanthemum, or perhaps we should rather say of pyrethrum. From the remarkable insecticide power of the flowers of this plant, known in trade as insect-powder, we might infer the presence of some active principle. The author has, in fact, isolated a paraffin, a new cholesterine, a glucoside, and an alkaloid which he has named chrysanthemine, and which is the chief subject of the memoir; pure chrysanthemine, a colourless syrup or colourless needles grouped in rosettes. The alkaloid may be heated for a long time on the water-bath, but above 100° it begins to decompose, giving off an odour of trimethylamine.

The aqueous solution has an alkaline reaction, both with turmeric and litmus papers. For its volumetric determination methyl-orange is preferable. The base is soluble in ethylic and methylic alcohol; it is insoluble in ether, chloroform, and benzene. Its salts behave as follows with the ordinary reagents for alkaloids. With bismuth and potassium iodide it gives a flocculent orange-yellow precipitate, which, on agitation, becomes crystalline and of a bright red colour. With mercury potassium iodide it yields a yellowish-white precipitate; with platinum-sodium iodide a brown precipitate; with gold chloride a yellow crystalline precipitate, which dissolves if heated and re-crystallises on cooling. With platinum chloride, mercuric chloride, picric and tannic acids, no precipitate is produced. Chrysanthemine is completely inactive in polarised light. Physiologically it is inoffensive. The author has experimented upon frogs, rabbits, mice, and dogs, and always found it completely inoffensive. Its formula seems to be $C_{14}H_{28}N_2O_3$.

Two papers treat of hydrogen peroxide; one by G. Giorgis examines the action of this compound and of water saturated with carbonic acid upon metallic magnesium. It results from his experiments that pure magnesium is oxidised in a minimum quantity by neutral hydrogen peroxide. The oxide resulting is scarcely soluble in pure water, whence the phenomena observed by Weltzier must probably have been due to some impurity in the materials. Pure water and oxygenated water saturated with carbonic acid convert magnesium into neutral carbonate. The aqueous solution of carbonic acid acts like a true acid.

A. Piccini has studied the action of hydrogen peroxide upon some oxyfluorides and fluorides. Santonine has also been made the subject of two elaborate papers, the one by P. Gucci and E. Grassi-Cristaldi, and the other by L. Francesconi.

Some of the contributors to this volume introduce numbers into the names of compounds, such as "On the hydrogenation of 1 phenyl, 4 methyl, 5 ethyl pyrazole, and on 1 phenyl, 3—5 dimethylpyrazole." Such a mode of notation can scarcely fail to prevent difficulties.

CORRESPONDENCE.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

SIR,—The communication of "F. G. M." in the last issue of the CHEMICAL NEWS has expressed the meaning of my letter exactly.

It would be a pity, I think, if a young chemist, after spending years in studying the science, should jump at the first opening that occurs, no matter what it be.

This, then, is where the difficulty comes in: which of the many branches of chemistry is advisable, speaking from a worldly as well as a scientific point of view?—I am, &c.,

W. S.

John Street, Glasgow.

GOLD IN SEA WATER.

To the Editor of the Chemical News.

SIR,—Recent paragraphs that have appeared in the press relating to the presence of gold (and other metals) in sea water, and referring to a patented electrolytic process or processes for obtaining such metals, include a statement that the quantity of gold has been estimated at one grain to the ton of sea water. Presumably, although my name does not appear in the paragraphs that friends have sent me, the statement of the proportion of gold in sea water is based upon my paper that appeared in the CHEMICAL NEWS (vol. xxvi., p. 159).

Not having the original paper at hand, I refer to "Watts's Dict. of Chem.," vol. vii., Second Supplement, and there find that my statement was that "the quantity is certainly less than one grain in a ton" of gold in sea water. I did not make any such statement as is now going the round: that a ton of sea water contains a grain of gold. I simply stated that proportion as an extreme possible limit.

I am the more particular to emphasize my old position of non-committal to a quantitative estimate of the gold in sea water, as experiments I have been for some months past making on sea water supplied from Lowestoft in kegs by the G. E. Ry. Co., convince me that the proportion of gold is not only much less than my former superior limit, but is also greatly less than I had supposed it to be. Nevertheless, of the presence of gold in sea water I have gained additional evidence: but a quantitative result I have not yet obtained.—I am, &c.,

E. SONSTADT.

Cheshunt, March 8, 1892.

The Preparation of Lackmoid.—M. Schaerger (*Schweits. Wochenschrift Pharmacie* and *Chem. Zeitung*).—The author causes sodium nitrite, without the addition of water, to act upon resorcine at a temperature not exceeding 110°. The product is dissolved in a little water, and freed from undecomposed resorcine by agitation with ether. Lackmoid forms a clear solution in water and dilute alcohol in any proportion. If the aqueous solution is mixed with acid, the red colouring-matter which results can be removed by agitation with ether. This character distinguishes lackmoid from the tincture of litmus.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 8, February 22, 1892.

Preparation of Amorphous Boron.—Henri Moissan.—The author uses for this purpose the action of metallic magnesium in powder upon an excess of boric acid, which must be absolutely dry. The product is a mixture of boron and of magnesium borate and boride. The borate and the chief part of the boride are eliminated by successive washings with acids. By a repeated treatment with boric acid in a state of fusion he oxidises the remainder of the boride, and after washing obtains amorphous boron, containing merely a very slight proportion of nitride. If it is desired to avoid the presence of these traces of boron nitride, we must operate in an atmosphere of hydrogen, or line the crucibles with titanic acid, and under these conditions the amorphous boron is obtained pure.

New Researches on the Monochlorised, Monobromised, and Monocyanised Aceto-acetic Ethers.—A. Haller and A. Held.—These researches show that, according to the mode of preparation, and therefore according to the reactions brought into play, the monohalogenous aceto-acetic ethers appear sometimes as compounds α, sometimes as γ derivatives, and sometimes as a mixture of substituted α and γ derivatives.

Researches on the Realisation of Spheroidal State in Steam-Boilers.—A. Witz.—Boutigny's phenomenon, the so-called spheroidal state of water, is not produced in boilers when the plates are in a state of incipient redness, but the evaporation reaches then a degree of activity which merits especial attention.

The Solubility of Tricalcic and Bicalcic Phosphate in Solutions of Phosphoric Acid.—H. Causse.—It appears that tricalcic phosphate dissolves in solutions of phosphoric acid to a much greater extent than bicalcic phosphate. The cause of this difference seems to reside in an equilibrium established between three factors—water, phosphoric acid, and monocalcic phosphate. The water seems to play the principal part; it distributes its action between the monocalcic phosphate and the phosphoric acid, and everything depends on the proportion of these two compounds.

On the Stereochemistry of Diacetyltartaric Acid. A Reply to a Communication by M. Le Bel.—Albert Colson.—A controversial paper which does not need to be reproduced.

Thermic Study of Sodium Isopropylate.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

On Tartronic Acid and the Potassium and Sodium Tartronates.—G. Massol.—The quantities of heat evolved by oxymalonic acid are greater than those disengaged under the same conditions by malonic acid. This result is conformable to those which the author has previously obtained on comparing malic and tartaric acids (oxysuccinic) with succinic acid.

Specific Weight of Textile Fibres.—Leo Vignon.—For determining these specific gravities the author uses the hydrostatic balance, employing instead of water pure benzene. Condensed gases were eliminated by means of a reduced atmospheric pressure. The specific gravity of cotton is given as 1·50; that of wool as 1·30, and that of silk in different states of preparation as 1·33. "Loaded" or weighted silks were found with specific gravities as high as 2·01.

Bulletin de la Société Chimique de Paris. Series 3, Vols. vii. and viii., No. 1, January 5, 1892.

The Molybdic Reaction of Oxygenated Water.—G. Denigès.—In the *Bulletin*, Series 3, Vol. vi., p. 22, M. Crismer enters into a discussion, historical and chemical, to prove that Schöne and himself had previously described this reaction, that it is untrustworthy and not sensitive, and that it is advantageous to employ his reagent (citric acid and ammonium molybdate). Crismer has, indeed, criticised about the end of 1888 the use of ammonium molybdate *acidulated* with sulphuric acid for the detection of oxygenated water. M. Denigès has shown that strongly sulphuric solutions have none of the disadvantages recognised by M. Crismer in solutions merely acidulated. M. Denigès therefore still recommends the following formula:—Dissolve 10 grms. ammonium molybdate in 100 c.c. water, and add, little by little, whilst refrigerating, 100 c.c. pure sulphuric acid. The liquid always takes a blue colour after some time, but the colouration disappears on heating. It is most sensitive at 60—80°. In practice we heat in a test-tube a few c.c. of the reagent, and add a few drops of the liquid in which oxygenated water is to be detected. In presence of this body there appears at once a yellow colour, which may even reach a deep orange. No other acid is to be used.

The Rotatory Power of Silk.—Leo Vignon.—This paper has been already noticed.

A Synthesis of Non-saturated Nitriles.—Edmond Fiquet.—The author has studied the action of metatoluic, cinnamic, and ethylic aldehyds upon cyanacetic acid. He points out that the ether obtained by Mr. Carrick, of the University of Leipzig, by the action of ethyl cyanacetate upon benzylic aldehyd in presence of sodium is not susceptible of the same transformation as that obtained by the author.

On Thiopinacone.—W. Spring and J. van Marsenille.—This compound has a composition answering to the formula C_8H_8S.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 69.

This issue contains no chemical papers.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Medical, 8.30.
— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).

TUESDAY, 15th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Peru—Its Commerce and Resources," by F. A. Pezet.

WEDNESDAY, 16th.—Society of Arts, 8. "Iceland," by Tempest Anderson, M.D.
— Meteorological, 7.
— Microscopical, 8.

THURSDAY, 17th.—Royal, 4.30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Progress of Romance in the Middle Ages," by Prof. W. P. Ker, M.A.
— Chemical, 8. "The Conditions which Determine Combination between the Cyanides of Zinc and Mercury and the Composition and Properties of the Resulting Double Salt," by Prof. Dunstan. "A Lecture Experiment to Illustrate the Phenomena of Coal-Dust Explosions," by Professor Thorpe, F.R.S. "The Ketone Formed by the Action of Dehydrating Agents on Camphor," by Dr. Armstrong and Dr. Kipping. "Platinum Tetra-chloride," by F. Pullinger, B.A.

FRIDAY, 18th.—Royal Institution, 9. "Modern Satire in Black and White," by George Du Maurier.
— Quekett Club, 8.

SATURDAY, 19th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

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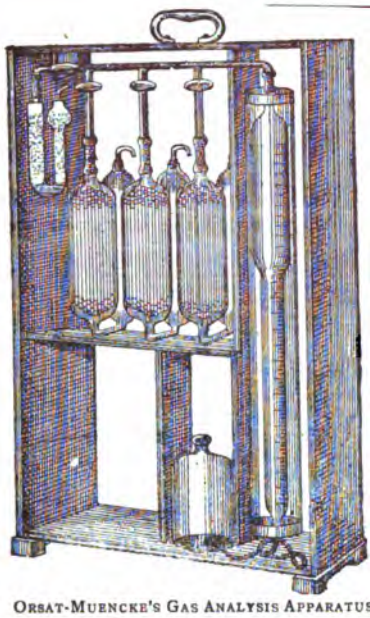

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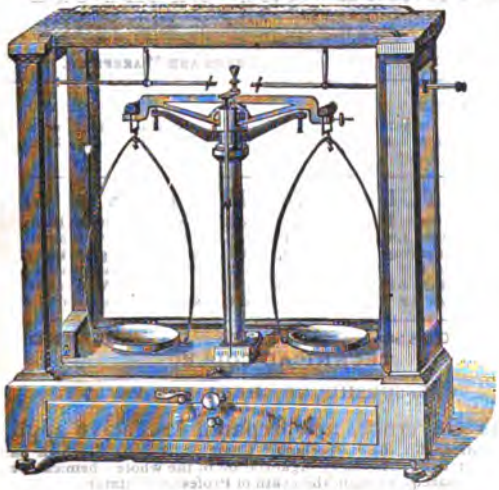

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VOL. LXV., No. 1686.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg.

Introduction.

UNDER this head we propose to give a series of papers concerning the modern crucible steel manufacture in Russia, describing also the preparation of projectiles, pattern castings, tool steel, locomotive tyres, &c.

In 1889 we superintended the erection of the crucible steel department of the Poutiloff Iron and Steel Works, St. Petersburg. The first thing built was a Siemens gas furnace with three compartments for ten crucibles each, and a muffle furnace for heating sixty crucibles at one time.

There was one gas-producer of the ordinary type, but only two compartments were fired, the other two always ready in case of some accident with the former. The consumption of coal (English) was 1·93 poods per pood of steel melted (1 pood = 40 pounds = 36·11 English pounds). We found that the best height for the layer of the coal was 32 inches, counting from the fire-grate. The run of the gas was then steady and quite sufficient for the melting of steel in due time.

During the making of hard steel (projectiles and tool steel) we had five castings per twenty-four hours, stopping melting on the evening of Saturdays and charging the crucibles again on Sunday mornings. But when steel castings were demanded, or medium hard steel was ordered, we made only four heats per twenty-four hours.

I had a great difficulty with the workmen, the crucible Siemens furnace being not in use in St. Petersburg. The Olouchoff Steel Works here, for the manufacture of their steel, principally for ordnance, use coke crucible furnaces and Siemens-Martin steel. I succeeded in getting some workmen formerly employed at these works, and in some two to three months my department went smoothly on.

Perhaps it may be interesting to state the amount of wages paid to the workmen. Such information respecting Russia is very scarce abroad. Each shift comprised one head melter, three crucible drawers, and one fireman for the muffle furnace and for the opening of the covers of the gas furnace during the casting. The ordinary workmen for bringing the crucibles to the moulds were in numbers according to the character of the cast made, and comprised the workmen employed in the department for other purposes (breaking cast-iron, shearing the raw materials, crucible making, &c.). Finally, the shift of the gas-producer consisted of one head workman and two firemen. The wages are in paper roubles.

Gas Furnace.

Head workman	2·40
Crucible drawer	1·60
Fireman (muffle furnace)	1·00

Gas Producer.

Head workman	1·15
Fireman	1·00

The workmen employed for bringing the crucibles on the average received 0·95 rouble. The piece-work wages for other work was as following (paper roubles) :—

	Per pood.
Modelling castings	0·60
Cleaning ,, ...	0·25
,, ingots	0·10
Shearing raw material	0·03
Breaking cast-iron	0·02
Cleaning used crucibles from slag	0·10

The charge of each crucible comprised sixty-two pounds of raw material. This material consisted of the following :—(*a*) Swedish cast-iron, brand "three lilies"; (*b*) Swedish iron, brand J. M.; (*c*) blister steel, Russian and Swedish (W.F.); (*d*) puddled steel, Russian (Beloretz Works); (*e*) acid and basic steel of the own Works; (*f*) old crucible steel from the market; (*g*) German ferro-manganese; (*h*) silicon pig-iron; and finally (*i*) silicon spiegel. The last two materials came also from Germany.

I prepared myself the ferro-aluminium (10 per cent of aluminium) by using cast-iron of good quality and pure aluminium received from the Pittsburgh Reduction Company, U.S.A. It contained, according to our analyses, 97·5 per cent of the metal.

I propose to deal in my next paper with the analyses of raw materials and the manufacture of crucibles. The third paper shall be on the melting of steel, and the fourth on the uses of crucible steel received.

NOTE ON THE ESTIMATION OF GOLD, TIN, AND CADMIUM IN ALLOYS.

By WILLIAM FRENCH, B.A., A.I.C.

DURING last autumn I had occasion to analyse some alloys containing gold, tin, and cadmium, and the method employed for separating the tin from the cadmium was that prepared by Löwenthal, viz., oxidising the solution of stannous chloride, and then warming up with a mixture of sodium sulphate and ammonium nitrate.

The oxide of tin frequently came down as a colloidal precipitate, which was extremely difficult to wash and collect, and the analyses required many hours for their completion. The filtrate from the oxide of tin was precipitated by sulphuretted hydrogen, and the cadmium sulphide washed to free it from ammonium and sodium salts, then dissolved in hot dilute hydrochloric acid. After filtering, the cadmium chloride was precipitated at the boiling-point with sodium carbonate; the cadmium carbonate filtered off and weighed as oxide in the usual manner.

As this method was tedious and lengthy I was led to try if other reagents could be used in place of ammonium nitrate, &c., and I find such a reagent in hydrogen peroxide which I have not yet seen anywhere described. My method consists essentially in adding hydrogen peroxide to a nearly neutral solution of the mixed chlorides of tin and cadmium, and warming. This precipitates the tin in a flocculent form, which readily settles and is capable of being filtered and washed with ease. The cadmium can then be precipitated direct from the filtrate with sodium or potassium carbonate.

A description of the analysis will make the above general statement clear. From one to two grms. of the alloy was heated with hydrochloric acid, using as little acid as possible to get the tin and cadmium into solution. The gold was next filtered off and weighed. To separate the tin from the cadmium, the filtrate was very nearly neutralised with potash, and from 4 to 5 c.c. of hydrogen peroxide (10 volumes) added; the whole, diluted to about half a litre with water, was then heated to the boiling-point. This throws down the tin in a very convenient form for filtering and washing; the precipitate after washing was dried, ignited, and weighed as SnO_2. The filtrate from the tin and washings were next evaporated to about half, and the cadmium precipitated at the boiling-point with potassium carbonate.

This method gives goods results with a mixture of tin and cadmium in solution, and also with the alloys I have tried is quite comparable with the other method, having the special advantage of a saving of at least half the time. Through the kindness of Messrs. Haycock and Neville I have been able to analyse some of their alloys, and here

give the analyses of two as compared with their analyses by the method mentioned by them (*C. J. S.*, lix., 936) :—

	Messrs. H. and N.	Modification.
(*a*).	Au = 3·51 per cent.	3·68 per cent.
	Cd = 9·86 ,,	10·13 ,,
	Sn = 86·31 ,,	86·19 ,,
(*b*).	Au = 29·16 per cent.	29·29 per cent.
	Cd = 13·83 ,,	13·91 ,,
	Sn = 56·67 ,,	56·82 ,,

Considering the method of preparation and object for which these alloys were made, it would be difficult to expect analyses to give more coincident results.

I am still studying the action of hydrogen peroxide as a means of separating tin from other metals.

University Chemical Laboratory,
Cambridge.

NOTE ON THE ANALYSIS OF SODIUM NITRITE.

By GEORGE LUNGE.

In the Chemical News, vol. lxv., No. 1684, p. 100, Messrs. Green and Evershed object to my method for estimating nitrous acid in sodium nitrite (which they otherwise acknowledge to be correct) as not giving accurate results in the presence of organic matter or other reducing substances. Since, however, as everybody knows, sodium nitrite is manufactured by fusing sodium nitrate with lead or copper, it would seem to be really very superfluous to take any account of organic matter or any other reducing substances in the present case. My method has been quite recently submitted to a totally independent examination by Professor Stutzer, of Bonn, and Dr. Reitmair (*Zeitsch. fur Angew. Chemie*, 1891, Part 22), who came to the conclusion that it is both easy of execution and perfectly correct.

Messrs. Green and Evershed prefer a method which they have published in 1886, and of which they believe they have been the first inventors. About eight years before their publication, however, I became acquainted with the identical method for testing nitrites, as being then in current use at several German colour works. I must point out that aniline hydrochloride was always employed then, not sulphanilic acid. I tried that method for myself, but rejected it as far more troublesome and far less accurate than the permanganate method. I remember perfectly well, when Messrs. Green and Evershed's paper came out, showing it to my demonstrator and remarking that their method lacked both novelty and usefulness. It is a mistake to say that I quote Baeckmann as the author of that method; I only quoted his handbook of technical analysis as my source for the description of the aniline method, as practised by the colour works' chemists, which description, by the way, is really identical with Messrs. Green and Evershed's way of proceeding (working with aniline and hydrochloric acid in an ice-cooled vessel, and testing by drops on iodised starch).

Apart from being decidedly inaccurate, the aniline method (letting alone sulphanilic acid) is at the best a tedious and troublesome process according to Messrs. Green and Evershed's own showing. You must start with absolutely pure dry anilines; you must work in a vessel cooled by ice; you must wait a few minutes after each addition of the nitrite solution, and a full hour after the last addition in order to see whether the reaction for nitrous acid does not vanish again.

You must take account only of a colour produced *at once* with the starch solution, as, on standing, the drop nearly always becomes blue. It is evident that sources of error are lurking all over here. Even Messrs. Green and Evershed themselves, who have probably more practice with their method than most other people, do not profess to have come nearer the true result, as indicated by Kinnicutt's method, than 0·4 per cent; but in the numerous tests made by myself and my students with the aniline method both before and after the appearance of their paper, we have not obtained anything like such good results.

I could not but come to the conclusion that both the aniline and sulphanilic acid methods, which have led to many disputes between buyers and sellers, must be rejected as misleading, whilst the permanganate method as modified by me gives absolutely uniform and correct results, with the very great advantage of each test requiring only a few minutes and being accurate even in less skilful hands. It is no matter of surprise that my method seems to have met with approval by the leading Continental manufacturers and buyers of nitrite of soda.

THE FERMENT OF THE OPIUM OF SMOKERS, AND ITS ARTIFICIAL FERMENTATION.

The smokers' opium, cleared of the rank and empyreumatic principles which this product contains in the raw state, cannot be offered for sale by the Régie until it has been subjected to a spontaneous fermentation, the duration of which is not less than ten to twelve months.

Chemical analysis has always been powerless to grasp the modifications which this fermentation causes, on account of their very complicated nature. We merely know that, in order to be consumable, the complete chandoo must be beaten in the air, then left in large vats for a long time. Its surface becomes covered little by little with a crust of moulds, which in some places swells, and in others sinks, grows wrinkled and dry. The opium has then acquired a kind of bouquet more or less delicate, which is appreciated by the smoker, and, in particular, it has lost the rank odour and acrid taste of burnt horn which characterise newly made opiums. Finally, the kneading of the paste becomes more easy, and the pipe is smoked without further delay.

M. Lalande, who, in 1890, published in the *Archives de Medicine Navale et Coloniale* a very complete account of the opium of smokers from a chemical point of view (which study was analysed in the *Revue* of August 16, 1890, p. 220), very judiciously ascribes this fermentation to aerial microbia; but he found it impossible to study the development of these microbia; he was merely able to observe that they existed, and he mentioned the scientific interest which a deeper study of the question might present.

The reading of this work suggested to M. Calmette the idea of utilising the resources of the Laboratory of Microbiology, at Saïgon, for the purpose of solving the problem posed by M. Lalande.

It was, in fact, apparent that it would be of great practical utility to endeavour to find methods for producing artificially the fermentation of opiums; as in industry they cause fermentation with beer barm in brewery malt. If this idea became feasible it would then be possible to obtain chandoos already fermented and fit for consumption in a relatively short time; one or two months, for example, instead of ten or twelve months; and the Custom House and Régies would thus immediately have at their command a capital of 1,500,000 francs, represented by the chandoo in course of spontaneous fermentation.

Besides this unproductive capital, the colony is not only exposed to the risk of fire and theft, but undergoes also, through slow evaporation of the opiums, a dead loss of some considerable extent, which rapid fermentation could avoid.

This is the method followed by M. Calmette as it is

described in the *Archives de Médecine Navale et Coloniale*, Feb., 1892:—

In artificial bouillons prepared with rinds of opium balls and heated at 120°, so as to destroy all foreign germs other than those he wished to sow, M. Calmette successfully isolated in the different opiums, in fermentation of various ages, a large number of microscopic vegetables belonging to the class of myzomycetes or lower order of fungi.

Bacteria, properly so called, are almost entirely absent in chandoos of good quality. We only find in some vats colonies of the *Bacillus subtilis*, a very common microbe in nature, and which thrives in most vegetable infusions. This microbe grows under the form of a wrinkled veil on the surface of the fats, depriving the sub-adjacent opium of the amount of air necessary for its normal fermentation in such a way that this last cannot take place until much later, when the *Bacillus subtilis* dies, having exhausted all the elements it could monopolise for its nutrition. It is then a question here of an opium parasite; a bad ferment which must be eliminated.

The best opiums are given by vats in which M. Calmette exclusively found *Aspergillus* and *Mucors*; the last much less numerous than the first. The *Aspergillus* belong to several species, but the most common are the *glaucus* and *niger*. In very old opium, considered as the best of the Régie, the author found perfectly pure cultures of the *Aspergillus niger*. It was then already indicated to try the artificial culture of this organism on new chandoo.

The *Aspergillus niger* easily grows in all acid mediums containing mineral elements in sufficient proportion, and its spores abound in the air of all hot or temperate climates. Its methodical culture based on the analysis of its peculiar chemical constitution was realised in France by M. Raulin, who for this object composed a very complicated liquid in which this microscopic vegetable grows with great rapidity and vigour.

This artificial liquid, employed by M. Calmette, is composed as follows:—

	Grms.
Water	1500
Sugar candy	70
Tartaric acid	4
Nitrate of ammonia	4
Phosphate of ammonia	0·60
Carbonate of potash	0·60
„ magnesia	0·40
Sulphate of ammonia	0·25
„ iron	0·07
„ zinc	0·07
Silicate of potash	0·07

If any of these eleven elements are suppressed, or the proportion limited, the culture of the vegetable falls off, and the weight of the plant furnished in the same time is much less. On this medium, in four days the liquid surface is entirely covered with a felted ramified mycelium supporting a multitude of small cylindric columns, on which are implanted black spherules with spores. These last, transported on the opium, easily germinate and run over all its surface, forming a velvety crust wrinkled over all its extent.

It is then very easy to cultivate the *Aspergillus* on the Raulin liquid; in the first place, to obtain the quantity of sowing required and with the spores obtained it only remains to sow the surface of the chandoo, which is to be put into a state of fermentation. Only, to obtain a rapid development of the vegetable, it will be necessary to operate in very wide flat vessels into which the air can easily enter. The thinner the layer of opium with regard to the surface, the more rapid will be the fermentation. Finally, the previous beating in the air, as practised by the Chinese empirically, has its reason of existence, because it multiplies the surfaces of the sowing, and also because it supplies the growing plant with a large amount of oxygen, very favourable to its growth.

The *Aspergillus* changes in a complex manner the composition of the chandoo at the various stages of its development. M. Calmette was able to observe its effects by syphoning under a layer of *lap lante* and, at various ages, the Raulin liquid, which he then replaced by other liquids containing, instead of sugar, dextrin or tannin.

We already knew that the *Aspergillus* secretes an inverting diastase, which at once transforms the sugar into glucose. The glucose is then burnt, and its last state is oxalic acid; dextrin undergoes the same change. M. Calmette was also able to observe that, if fresh, chandoos sometimes contain more than 6 per cent of glucose, opium in which fermentation has ended only contains traces, which can hardly be perceived with the Fehling liquid or the polarimeter. The dextrin has completely disappeared. The tannin is entirely changed into gallic acid by the adult *Aspergillus*, but this transformation only occurs during sporulation of the plant. It is here a question of a division produced by the hydration of the tannin under the action of the diastases of the *Aspergillus*. M. Calmette found that in a porcelain basin covered with a plate of glass, ten days of fermentation were sufficient to take away all the tannin of a solution of 20 grms. per 300.

As for oxalic acid, produced by the combustion of the glucose and dextrin, it is again met with in the meshes of the mycelium in the form of oxalate of lime. The felted layer of the *Aspergillus* imprisons a multitude of microscopic crystals of this salt, of which the form is like that of an envelope for letters.

It does not appear either that the alkaloids are changed in their proportions by the development of the vegetable.

From a practical and even industrial point of view, perfect fixity of the quantities of alkaloids is only of minor importance. It is of little consequence to the smoker, in fact, whether the opium of the Régie contains 6 or 8 per cent of morphia; with about 2 grms. per cent he does not experience any difference in the effects on his organism. On the contrary, he can quite appreciate a pleasing flavour and sweet perfume in the opium, its burning well, its not igniting and drying too much in swelling. These qualities opium only acquires by fermentation, as it does not possess them at the time of its leaving the distillery.

The chief thing for the Régie is to obtain, as soon as possible, a completely fermented chandoo, and the laboratory experiments undertaken by M. Calmette demonstrate that this result can be attained in a maximum delay of one month. At the end of this time, the diastases of the *Aspergillus* have given their useful effect, the glucose and dextrin contained in the chandoo are destroyed, and the tannin transformed into gallic acid. Opium is then fit for consumption, and the tastings submitted to smokers' experts gave as result that the product of artificial fermentation has the qualities of old opium already some years of age; qualities which are much prized by the Chinese.—*Revue Scientifique*, Feb. 27, 1892.

ALUMINIUM SULPHIDE.

By H. N. WARREN, Research Analyst.

This compound, the production of which according to the numerous authorities upon the subject is brought about by the action of sulphide of carbon upon Al_2O_3 at a red heat, is said to possess a glassy appearance, to be fusible at a red heat, and instantly decomposed by water. Following up these statements and requiring this substance for further investigation the author has taken pure Al_2O_3, prepared by dissolving the metal in HCl, evaporating to dryness, and calcining the same; this was subjected for about twenty minutes to the action of CS_2 aided by a full red heat; upon cooling, and withdrawing the same from its porcelain enclosure, the alumina remained unaltered,

even retaining its usual whiteness. This I was not surprised to discover, for future experience with this compound had led me to believe that alumina and also carbon disulphide were far more stable substances than these plausible theorists assert. Nothing daunted, however, I determined to give the trial every advantage, and urged the heat to whiteness for a full hour, meanwhile maintaining a rapid stream of gaseous carbon disulphide. Upon cooling and examining the contents, I soon discovered that I had to deal again with pure Al_2O_3. Amongst various other suggestions I was led to consider the difficulties of producing pure alumina when precipitated from a solution of alum. Having procured a solution of potash alum, I precipitated the alumina contained therein by the addition of an excess of ammonia, washing the precipitate until free from sulphates, drying the hydrate thus obtained, and calcining to Al_2O_3, with repetition of the former process.

Upon re-examining I now discovered the glassy melted mass which had been formed, which presented a strong odour of SH_2 when thrown into water. Upon more careful examination I discovered that after all I had only formed, instead of aluminium sulphide, a very small quantity of potassium sulphide, which my alumina had mechanically carried down as sulphate; but which, owing to the high temperature the whole had been subjected to, had naturally induced partial fusion. Is this the aluminium sulphide described by Fownes, revised by Gmelin, and most other supposed authorities? I am inclined to believe that it is as plausible as treating a mixture of Al_2O_3+Cu+C in order to obtain aluminium bronze (Watts's "Dictionary of Chemistry"), which experiment, when subjected to the oxhydrogen furnace, resulted in pure copper (perhaps electricity would favour it a little).

Several other such results could be quickly enumerated, but the foregoing will perhaps be sufficient to encourage scepticism. To prepare aluminium sulphide subject aluminium at a red heat to the action of sulphur vapour.

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ACTION OF NITRIC ACID ON ASPHALT AND CELLULOSE.

By REGINALD A. FESSENDEN.

In view of the experiments of Luzi and Friswell on the action of nitric acid on graphite and coal, the following account of two substances which I prepared for commercial purposes may be of interest:—

Some years ago, in consequence of certain patent litigation, Mr. Edison requested me to find some non-fibrous substance suitable for lamp filaments which should have the same or greater efficiency than those made of bamboo. A great variety of new substances was prepared, and two of these seem worth description. Asphalt was taken and dissolved in chloroform. It was then treated with dilute nitric acid and the whole heated; the chloroform was then distilled off. The substance produced was dissolved in the chloroform and treated once more with stronger acid, and the chloroform was then distilled off again.

The residue was a light brown substance if the acid had been of a proper degree of dilution. If the acid had been too strong, the substance was of a shiny black colour, due to the formation of a secondary product. This secondary product is soluble in alcohol, and may be separated by dissolving the substance left after the distillation in chloroform and then adding alcohol. The light brown substance is then precipitated in a pure state. This latter when heated chars without swelling or puffing, and turns to a very hard dense charcoal. If any traces of the black substance are left, it puffs up very much. The black substance seems to be a compound containing nitrogen. The brown substance is insoluble in most of the ordinary solvents, but is dissolved by chloroform and a few of the essential oils, such as oil of birch. On being triturated with choralhydrate, the mixture turns to a thick liquid. In manufacturing the filaments, a thick paste of the light brown substance and chloralhydrate was squirted through a dye into filaments, which on being carbonised at a very high temperature shrunk considerably, and made a filament much more durable and economical than any hitherto produced. The filament was so elastic that it could be tied into a knot of $\frac{1}{32}$ of an inch diameter, and was strong enough to penetrate the skin like a needle.

The second substance was formed by treating cellulose with dilute nitric acid, thereby forming the oxy-cellulose of Messrs. Cross and Bevan. This oxy-cellulose is soluble, on digestion, in ammonia, and on evaporating the solution a transparent film is left, which by its odour when burnt seems to be nitrogen compound of cellulose; it very strongly resembles gelatin in appearance, flexibility, and odour when burnt, and might, on account of its solubility in ammonia, be of use for photographic plates.

On account of the pressure of work at the time no analysis was made of either of these compounds.

THE SEPARATION OF BISMUTH AND CADMIUM.

By PAUL JANNASCH and P. ETZ.

In the separation of certain metals of the sulphuretted hydrogen group, such as lead, bismuth, cadmium, and tin, according to the customary methods, we not seldom encounter unexpected difficulties which seriously affect the accuracy of the results. More trustworthy are evidently separations in a current of chlorine, most of which have already been studied.

The decided advantages which bromine permits of in its use, as well as my observation that the temperatures of volatilisation of the metallic bromides differ more widely among themselves than those of the corresponding chlorides, induced me to re-examine the analyses which I effected some years ago with bromine-vapour, and to extend the method. The first investigation of this kind, undertaken in concert with Herr P. Etz, fell out so favourably that we could hope by means of our new process to enrich quantitative analysis with a series of exceedingly simple and accurate metallic separations.

Our procedure was the following:—As initial material, we used cadmium sulphate and metallic bismuth, of the purity of which we satisfied ourselves by especial analyses. These substances were dissolved in nitric acid, the solution evaporated down on the water-bath, and the residue taken up with as much hydrochloric acid as was necessary to prevent the deposition of basic bismuth chloride on the addition of about 100 c.c. of water. From this solution, which was heated to ebullition, the metals were thrown down as sulphides by means of a current of sulphuretted hydrogen, collected upon a filter, dried, and weighed at 100°, washed with hot sulphuretted hydrogen water, and then completely dried in an air-bath and weighed.

The desiccated mixture of sulphides was placed in a porcelain boat in a dried tube of potash-glass, and a brisk current of air, which had traversed a cylinder containing bromine, was passed over it from a gasometer. The bromine acts upon the substance even in the cold, but the reaction must be assisted and completed by moderate heating with a gas flame 1½ inches in height kept in a wavering motion, during which we may observe in the tube the occasional appearance of a russet-yellow flame.

After about half an hour, all the bismuth has been carried into the receivers, which have been charged with weak hydrochloric acid, whilst all the cadmium remains behind in the boat as a bromide. This bromide is dis-

solved in a little dilute hydrochloric acid, heated to ebullition, and precipitated with sodium carbonate. The solution of bismuth taken from the receivers was evaporated down, and this operation was repeated two or three times after adding nitric acid, in order to eliminate the hydrochloric acid, which would interfere with the subsequent precipitation. In their future operations the authors will fill the receivers with very dilute nitric acid instead of hydrochloric acid. The bismuth is finally separated by boiling with a mixture of ordinary ammonium carbonate and a little ammonia.

The complete separation of the bismuth appeared on the careful examination of cadmium. No trace of a brown precipitate appeared on passing sulphuretted hydrogen into the hydrochloric solution. The precipitate was a pure yellow from the first. Moreover, the solution of cadmium, copiously diluted with water, gave no milky turbidity of bismuth oxychloride.

The mixed sulphides must be perfectly free from water when exposed to the action of the current of vapour of bromine. —*Berichte der Deutsch. Chem. Gesell.*, xxiv. p. 3746.

THE SEPARATION OF BISMUTH AND LEAD.

By P. JANNASCH and P. ETZ.

After obtaining so favourable results with the separation of bismuth and cadmium in a current of bromium vapour and air, we endeavoured in the same manner to effect a trustworthy quantitative separation of bismuth and lead. The fact was confirmed that the products of volatilisation of the metallic bromides lie relatively more remote from each other (as regards the temperature of volatilisation) than the corresponding chlorides. Hence there is no difficulty in volatilising bismuth in presence of lead by merely heating their sulphides in a current of bromiferous air with a gas-flame 1½ inches in height.

In the execution of our method metallic bismuth and pure lead nitrate were dissolved in pure nitric acid, the metallic salts were evaporated to dryness, again taken up with water, and the necessary quantity of hydrochloric acid, the rather dilute solution is precipitated whilst hot with sulphuretted hydrogen, the precipitated sulphides are dried at 100°, placed in a porcelain boat which has been previously weighed, and heated in a current of air and bromine vapour. Bismuth bromide distils over completely, whilst lead bromide remains in the boat in a state sufficiently pure for weighing. The receivers for the bismuth bromide contained very dilute nitric acid.

For success the following precautions are absolutely necessary. The sulphides obtained must not be allowed to stand a long time, either in the liquid or in the funnel, &c., but the operation must be proceeded with as soon as possible. We have observed that a too prolonged action of the air upon the mixed sulphides is decidedly injurious and sometimes may lead to results which are completely worthless. Such preparations when subsequently heated in the current of bromine vapour do not yield simply pure bromides, but simultaneously basic compounds,—a circumstance which more or less interferes with the complete volatilisation of the bismuth. We therefore made the following arrangement. In the evening the solution was placed ready for the introduction of the sulphuretted hydrogen, so that the precipitation may be effected without loss of time the next morning. The filter is carefully lifted out of the funnel and dried, first on a flat porcelain capsule, and then in the funnel, so that in the afternoon, after the commencement of the analysis, we were able to undertake the heating in a current of bromine vapour. The expulsion of the bismuth by bromine succeeded best when a somewhat abundant quantity of sulphur was mixed with the precipitated sulphides. Hence it is advantageous to add to the hydrochloric solution of the metals a few drops of red, fuming nitric acid, prior to the introduction of the current of sulphuretted hydrogen.

The mixed sulphides in the porcelain boat, before their introduction into the glass tube, should be duly comminuted by means of a platinum rod, in order, on the one hand, to admit of a rapid and thorough-going action of the bromine, and on the other to prevent the projection of particles, which is apt to occur if the mass consists of large fragments.

The current of bromine from the very commencement of the operation should be rather rapid (about 300 gas bubbles per minute from a glass tube of 6 m.m. in width, since a deficiency of bromine may interfere with the formation of the volatile bismuth tribromide, and may also allow of sublimation in the wrong direction. At the end of the operation, and whilst the tube is cooling, the current may be moderated accordingly.

As it is found disadvantageous to leave the mixed sulphides in the drying-closet at 100° too long, it is better to put an end to the desiccation as soon as the loss of weight of the substance does not exceed a few m.grms. in a quarter of an hour. Hence it appears necessary before commencing the bromine treatment to pass first a current of dry air over the substance in the boat at a very gentle heat, so that the moisture still present may be carried over into the receiver.

In the treatment with bromine an unnecessarily strong heat must be avoided. A Bunsen flame of 8 c.m. in height is sufficient. The tube is first heated in front of the boat, waving the flame to and fro, and then the boat itself is gradually heated until the residual lead bromide melts. When all the bismuth has been driven as far forward as possible the flame is brought back to the boat, its contents being again heated to fusion. This is repeated two or three times, and when nothing further passes over, the heat must not be increased, but the contents of the tube are allowed to cool quietly in the current of bromine.

The lead is weighed first as bromide in the boat and finally as sulphate, into which state it is converted by heating the bromide with saturated chlorine water and precipitating the solution of lead chloride with sulphuric acid.

The solution of bismuth nitrate in the receivers is concentrated, precipitated at the temperature of ebullition with ammonium carbonate, and weighed as bismuth oxide. The ignited oxide is covered with solution of ammonium carbonate, evaporated on the water-bath, heated more strongly in an air-bath, and fully ignited to expel any traces of sulphuric acid.—*Berichte der Deutsch. Chem. Gesell.*, vol. xxv., p. 124.

ON A SERIES OF NEW COMPOUNDS—CHROMOSULPHURIC ACID AND THE METALLIC CHROMOSULPHATES.

By A. RECOURA.

In a recent memoir I described the preparation and the properties of a compound isomeric with chromium sesquisulphate, $Cr_2 3SO_4$, which I named provisionally green chromium sulphate, although it neither presents the characters of a sulphate nor those of a salt of chrome. I have shown, in fact, that this compound does not admit of double decompositions; thus its solution does not precipitate barium chloride as do all the sulphates. Hence I concluded that this compound is not a salt, but a compound of a peculiar nature.

I purpose demonstrating in this paper that a mol. of this compound may combine with a mol. of sulphuric acid or of any metallic sulphate, forming compounds such as $Cr_2 3SO_4, SO_4H_4$ or $Cr_2 3SO_4, SO_4K_2$, or, again, $Cr_2 3SO_4, SO_4Zn$, &c.,—compounds in which all the sulphuric acid is masked, that of the metallic sulphate as

well as that of the chromium compound; whilst, on the contrary, the metals K, Zn, &c., may be shown by the ordinary reagents, so that we may consider these compounds, which are neither sulphates nor salts of chrome, as salts of a peculiar acid $(Cr_{24}SO_4)H_2$, an acid having a complex radicle like the chromocyanhydric acid, and which I call chromosulphuric acid.

The fundamental experiment which establishes the existence of these compounds is the following:—We mix a solution containing 1 mol. of the compound $(Cr_{23}SO_4)$ with a solution containing 1 mol. of sulphuric acid or of any metallic sulphate whatever, *e.g.*, a mol. of copper sulphate. Combination takes place immediately; for if we pour barium chloride into the liquid thus obtained we observe no precipitate. The liquid therefore contains no sulphate, the sulphuric acid of the sulphate being entirely involved in the chromic radicle. The liquid no longer presents the reactions of a chromic salt, though it yields those of the salts of copper; it is therefore a solution of copper chromosulphate, $(Cr_{24}SO_4)Cu$.

The radicle of these salts is unstable, that is, only in the dissolved chromosulphates. After the lapse of half an hour or sometimes less, according to the nature of the compound, the solution begins to be precipitable by barium chloride; it is precipitated immediately if heated to ebullition. To observe the absence of the production of barium sulphate it is necessary to operate only with very dilute solutions, otherwise the chromic radicle is decomposed and a precipitate is formed.

The following are the methods of preparing these salts in the solid state and their properties:—

Chromosulphuric acid, $(Cr_{24}SO_4)H_2,11H_2O$).—To obtain this compound in the solid state I reduce chromic acid with alcohol in presence of a suitable quantity of sulphuric acid and the smallest possible quantity of water. As this process is delicate I will describe it in detail. I mix 50 grms. of chromic acid with 25 grms. of water and 50 c.c. of concentrated sulphuric acid. I pour into this mixture drop by drop 15 c.c. of alcohol at 95 per cent, taking care that the temperature does not rise above 30°. I thus obtain a green syrup, which is drained to separate it from unreduced chromic acid; it is then ground up in a mortar with an equal volume of crystallisable acetic acid. This precipitates the chromic acid from its solution, and there is obtained a green paste which is rapidly drained on the Sprengel pump to separate the acetic acid. The compound is then left in a vacuum until it is inodorous.

We obtain thus a green powder, $(Cr_{24}SO_4)H_2,11H_2O$. This is chromosulphuric acid, which is very hygroscopic and deliquesces rapidly in moist air. But in dry air it may be preserved indefinitely; its solution is very unstable. This instability is due on the one hand to its slight formation heat, and on the other to the instability of the compound $Cr_{23}SO_4$, which as soon as formed begins to transform itself into the violet chrome sulphate. This instability of chromosulphuric acid in solution is manifested in various ways. In the first place the solution, which is at first of a fine green, turns by degrees to blue. After some days it is merely a mixture of violet chrome sulphate and of sulphuric acid.

Potassium Chromosulphate, $Cr_{24}SO_4K_{24}H_2O$. — In order to obtain this compound in the solid state we must not attempt to crystallise its solution. The most simple method is to partially dehydrate by heat chrome-alum. This compound is kept for some hours at 90°, when it loses 12 mols. of water. It is then kept at 110° until it only contains 4 mols. of water. We thus obtain a green powder, which is potassium chromosulphate. Sodium chromosulphate, $[Cr_{24}SO_4]Na_{10}H_2O$, is prepared similarly to the potassium salt.

Ammonium chromosulphate, $[Cr_{24}SO_4](NH_4)_{25}H_2O$, is prepared like the former. It is a pale green powder which dissolves in water in a few minutes. The alkaline chromosulphates are prepared also by a second method, which consists in reducing a mixture of bichromate and sulphuric acid and sulphuric acid with alcohol as in preparing chrome-alum, but in presence of a very small quantity of water.—*Comptes Rendus*, vol. cxiv., p. 477.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 3rd, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MESSRS. G. P. Darnell Smith, Ernest J. Parry, Robert Ludwig Mond, W. P. Hatton, and W. J. A. Butterfield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Price Dodds, 3, Eversley Place, Heaton, Newcastle-on-Tyne; Henry Ellison, Whitechapel Road, Cleckheaton; Albert Augustus Lintern, High Scnool, Middlesbrough; Herbert Edward Lindley, 13, St. Bartholomew Road, Camden Road, N.; John Northing, 96, Tretonville Road, Sandymount, Co. Dublin; Frederick J. Oldershaw, 34, Bramhall Lane, Stockport; Albert Ernest Richardson, 4, Black Hall Road, Oxford; James Stenhouse, Tanfield, Inverleith Row, Edinburgh.

Address to Professor Bunsen.

It was announced that it was proposed to present an Address to Prof. Bunsen, who has now been fifty years a Foreign Member of the Society, and that among those who sign it all those who have been his pupils should, as far as possible, be included. (See p. 121).

Of the following papers, those marked * were read:—

*112. "*A Rule for Determining whether a Given Benzene Mono-derivative shall give a Meta-di-derivative or a Mixture of Ortho- and Para-di-derivatives.*" By Professor CRUM BROWN and Dr. GIBSON.

The rule suggested will be understood after reference to the accompanying table (see next page).

It will be seen that whenever the *hydride* of the radicle (column C) contained in the mono-derivative (column A) is asterisked, column E shows that a mixture or ortho- and para-di-derivatives is formed, and that whenever the *hydroxide* of the radicle (column D) contained in the mono-derivative (column A) is asterisked, column E shows that the meta-derivative is obtained.

The substances marked with an asterisk in column C are such hydrides as are *not* convertible by *direct* oxidation into the corresponding hydroxides in the next column whereas those asterisked in column D are compounds which can be formed by direct oxidation from the corresponding hydrides; the rule is based on this distinction.

DISCUSSION.

Mr. GROVES having referred to the statement which was on record that hydrogen chloride was oxidisable to hypochlorite by permanganate,

Prof. THORPE said that this was an error, and arose from the use of impure permanganate, made by the old-fashioned method with the aid of chlorate.

Dr. ARMSTRONG remarked that the rule suggested might be regarded as a modification of the usual statement that derivatives containing *acid* radicles gave meta-derivatives, since not only NO_2, SO_3H, CO_2H, but also COH and COR, might be ranked as acid radicles. In neither form, however, did the rule apply to such a case as that afforded by dimethylaniline, which yield much meta-derivative.

*113. "*The Relative Orienting Effect of Chlorine and Bromine.* (I.) *The Constitution of Parabrom- and Parachlor-Anilinesulphonic Acids.*" By HENRY E. ARMSTRONG and J. F. BRIGGS.

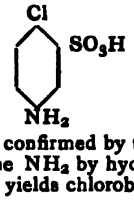
The case studied is that afforded by parachlorobromobenzene; it is found that when sulphonated this yields a uniform product characterised by a sulphochloride melt-

A.	B.	C.	D.	E.
C_6H_5Cl	$\cdot Cl$	HCl*	$HOCl$	*o-p.*
C_6H_5Br	$\cdot Br$	HBr*	$HOBr$	*o-p.*
$C_6H_5CH_3$	$\cdot CH_3$	HCH_3*	$HOCH_3$	*o-p.*
$C_6H_5NH_2$	$\cdot NH_2$	HNH_2*	$HONH_2$	*o-p.*
C_6H_5OH	$\cdot OH$	HOH*	$HO\cdot OH$	*o-p.*
$C_6H_5NO_2$	$\cdot NO_2$	HNO_2	$HO\cdot NO_2$*	*m.*
$C_6H_5CCl_3$	$\cdot CCl_3$	$HCCl_3$*	$HO\cdot CCl_3$	*o-p.*
$C_6H_5CO\cdot H$	$\cdot CO\cdot H$	$HCO\cdot H$	$HO\cdot CO\cdot H$*	*m.*
$C_6H_5CO\cdot OH$	$\cdot CO\cdot OH$	$H\cdot CO\cdot OH$	$HO\cdot CO\cdot OH$*	*m.*
$C_6H_5SO_2\cdot OH$	$\cdot SO_2\cdot OH$	$HSO_2\cdot OH$	$HO\cdot SO_2\cdot OH$*	*m.*
$C_6H_5CO\cdot CH_3$	$\cdot CO\cdot CH_3$	$HCO\cdot OH_3$	$H\cdot CO\cdot CH_3$*	*m.*
$C_6H_5CH_2\cdot CO\cdot OH$	$\cdot CH_2\cdot CO\cdot OH$	$H\cdot CH_2\cdot CO\cdot OH$*	$HO\cdot CH_2\cdot CO\cdot OH$	*o-p.*

ing at 66°, which crystallises in massive, prismatic plates very similar to paradibromobenzene sulphochloride, the corresponding amide melting at about 178° (uncorr.).

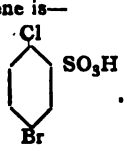
To determine the constitution of this product, the amido-acids prepared by sulphonating parabromaniline and parachloraniline were converted into chlorobromobenzenesulphonic acids; they gave isomeric acids, as should be the case if they were of corresponding constitution, the acid prepared from parachloranilinesulphonic acid being identical with the product from chlorobromobenzene.

According to Claus and Mann (*Annalen*, cclxv., 92), parachloraniline yields two isomeric acids on sulphonation, one being formed in but small quantity. The authors have been able to obtain only one acid; they have, indeed, observed that no fewer than three distinct forms of crystals separate from the aqueous solution of the product—long, striated rods springing from a common centre; rectangular, apparently rhombic prisms; and rhombs, probably monoclinic, which rapidly become opaque on exposure to air; but these appear to be all one substance, the difference in form being conditioned by difference in the amount of water of crystallisation. Claus has assigned the formula—



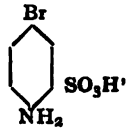
to the acid. This is confirmed by the authors, who find that, on displacing the NH_2 by hydrogen by the hydrazine method, the acid yields chlorobenzene*ortho*sulphonic acid.

Hence it follows that the acid formed by sulphonating parachlorobromobenzene is—



It would seem, therefore, that the chlorine rather than the bromine "attracts" the sulphonic group; but it will be necessary to ascertain whether the isomeric acid is not perhaps a less stable form, in which case it may be that the final product is not merely the product of direct sulphonation.

The chlorobromo-acid prepared from parabromanilinesulphonic acid yields a sulphochloride crystallising in ill-defined plates melting at 46°, the corresponding amide melting at about 191° (uncorr.); the fact that it is different from the chlorobromo-acid prepared from parachloroanilinesulphonic acid is in itself conclusive evidence that the acid obtained from parabromaniline is not—



as Borns asserts, but that it corresponds in constitution to the acid prepared from parachloraniline, as might indeed be expected to be the case. Borns (*Annalen*, clxxxvii., 372) bases his conclusion as to the constitution of the acid on its conversion by displacement of the NH_2 group by hydrogen into bromobenzene*meta*sulphonic acid, but no proof that he was dealing with this and not the ortho-acid is given beyond that contained in the bare statement that his product was recognised as the meta-acid from the composition and properties of the potassium and barium salts, the chloride (oily) and amide (m. p. 154°). The bromosulpho-acid obtained by the authors, however, yields an amide melting at about 183°, and is, undoubtedly, the ortho-acid. Parabromanilinesulphonic acid crystallises in three distinct forms closely resembling those in which the parachloro-acid crystallises.

Discussion.

The President remarked that it was usually supposed that NH_2, like OH, had a powerful directing influence, and therefore it appeared remarkable that para-brom- and chlor-aniline should yield sulphonic acids in the formation of which this influence of the NH_2 group apparently did not come into play.

Dr. Armstrong, in reply, said he thought it probable that in consequence of the formation of sulphate, the NH_2 group was rendered ineffective, and as the para-position is blocked by it, necessarily an ortho-chloro- or bromo-sulphonic acid was formed.

*114. "*Notes on Anhydrides of Sulphonic Acids.*" By Henry E. Armstrong.

Hitherto but little attention has been paid to this class of compounds: not long after Hübner, in 1884 (*Annalen*, ccxxiii., 238) had described a series of somewhat unsuccessful attempts to prepare phenylsulphonic anhydride, Abrahall succeeded in obtaining this compound by interaction of phenylsulphonic chloride and silver phenylsulphonate (*cf. C. S. Trans.*, 1886, 692); he desuribes it as crystallising from chloroform in fine prisms melting at 54°, and as being extremely deliquescent. Meanwhile it had been observed in Victor Meyer's laboratory that a number of bromo- and chloro-derivatives of thiophene, as well as paradibromobenzene and 1 : 2 : 4-tribromobenzene, gave sulphonic anhydrides directly on treatment with pyrosulphuric acid, all the anhydrides thus obtained being remarkable on account of their very slight solubility, even in boiling water, and the difficulty with which they were hydrolysed (*cf. Berichte*, 1886, 652).

In the course of the experiments with parachlorobromobenzene, referred to in the previous abstract, it was noticed that whereas this was wholly converted into sulphonic acid by so-called 100 per cent acid, a fuming acid containing about 20 per cent of anhydride gave as chief product a microcrystalline anhydride similar to that prepared by Rosenburg from paradibromobenzene. On contrasting the behaviour of paradichloro-, chlorobromo-, and dibromo-benzenes with such fuming acid, it was found that the dichloro- gave relatively the smallest, and the dibromo-derivative the largest, yield of anhydride, monochlorobenzene yielding only sulphonic acid and sulphone. It therefore seemed probable that the anhydride was a

secondary product formed by dehydration of the sulphonic acid under the influence of the sulphuric anhydride: and that this is the case is shown by the fact that if, for example, potassium dibromobenzenesulphonate be mixed with fuming sulphuric acid, it is converted into the corresponding anhydride. To judge from a statement made by Bässmann (*Annalen*, cxci., 213), it would seem that, in some cases, such anhydrides may be precipitable even from aqueous solutions of sulphonates. Obviously there are the same differences between sulphonic acids as between carboxylic acids with regard to the readiness with which they undergo dehydration.

*115. "*Contributions to the Knowledge of the Aconite Alkaloids.* Part II. *The Alkaloids of true Aconitum Napellus.*" By Professor DUNSTAN and Mr. JOHN C. UMNEY.

The authors have examined the alkaloids of true *Aconitum napellus* plants grown by Mr. E. M. Holmes at the instance of the British Pharmaceutical Conference. The alkaloids were extracted from the roots by the following process, which precludes the possibility of the occurrence of hydrolysis, &c.:—The solution obtained by percolating with cold rectified fusel oil (b. p. 100—132°) was agitated with water acidified with 1 per cent of sulphuric acid, and the resin having been removed by extracting the acid solution so obtained with chloroform, the liquid was made just alkaline with dilute ammonia and extracted with ether, which dissolved out a considerable quantity of alkaloid, but left in solution a further and smaller quantity, which was subsequently extracted by agitation with chloroform. The *alkaloid soluble in ether* was obtained as a gum-like mass incapable of crystallisation. By conversion into bromhydride it was separated into a crystallisable and an uncrystallisable salt.

The crystalline product was identified as the salt of aconitine, the crystalline and highly toxic alkaloid already described by one of the authors and Dr. W. H. Ince (*C. S. Trans.*, 1891). The alkaloid separated from the pure bromhydride melted at 188·5° (corr.), and afforded on combustion numbers agreeing with the formula—

$$C_{33}H_{45}NO_{12}.$$

The specific rotation of the bromhydride in aqueous solution was ascertained to be $[\alpha]_D - 29{\cdot}65$, a value which agrees with that previously recorded. As some doubt exists as to the solubility of aconitine in water, a determination was carefully made with this pure specimen. The mean of two determinations gave 1 grm. in 4431 grms. of water as the solubility at 22°; Jürgens had previously recorded the far greater solubility of 1 in 745 at the same temperature.

The non-crystalline bromhydride furnished a gummy alkaloid soluble in ether and alcohol, but only sparingly soluble in water, the aqueous solution being alkaline to litmus, and very bitter, but not giving rise to the tingling sensation so characteristic of aconitine. Not only the alkaloid, but also the chlorhydride, sulphate, nitrate, and aurichloride prepared from it could not be crystallised. This alkaloid is not identical either with aconine or with the picraconitine of Wright and Luff. A full account of it will be given in a later paper, considerable progress having already been made in the most difficult task of isolating it in a pure state. The authors propose to assign to it the name *napelline*, which was first given to the alkaloid now known as pseudaconitine, and afterwards by Hübschmann to a substance which the work of Wright and Luff showed to be a mixture chiefly composed of aconine. The napelline obtained in the manner described is probably associated with another amorphous alkaloid about which they have at present little information to give beyond the fact that neither it nor its salts appear to crystallise.

The *alkaloid soluble in chloroform* was proved to be *aconine*, the compound which is obtained together with benzoic acid on hydrolysing aconitine.

The roots of true *Aconitum napellus*, therefore, must be held to contain three alkaloids, one of which is crystalline, viz., aconitine, two being amorphous, viz., napelline and aconine. Indications have been obtained of the presence of a fourth alkaloid, which is amorphous and closely resembles napelline.

The authors find that the juice expressed from the roots contains a large proportion of amorphous bases but very little aconitine, the greater part of this latter remaining in the root, from which it may be extracted, together with the remainder of the amorphous alkaloids, by exhausting with amyl alcohol. The total quantity of amorphous alkaloid obtained amounted to more than twice that of aconitine.

The physiological action of the alkaloids referred to is being investigated. The results so far obtained point to the conclusion that crystalline aconitine is by far the most toxic alkaloid contained in *Aconitum napellus*.

(To be continued.)

INSTITUTE OF CHEMISTRY.

THE Annual General Meeting was held at Burlington House on Tuesday, March 1, 1892, under the presidency of Dr. TILDEN, F.R.S. A strong muster of members was caused by the expectation of a lively meeting, it being known that opposition to the "house" list for the new council had been organised. The first business was the treasurer's report, which showed a large invested capital. The first "passage of arms" was initiated by Mr. C. T. KINGZETT, whose inquiry for the details of an item of £50 for "taking notes" of a conference in May last, but which were never issued to the members, was met by an emphatic refusal from Mr. DAVID HOWARD, the treasurer, and the PRESIDENT judiciously remarked that the account had been duly audited, that the council, and not the treasurer, was responsible, and that anybody could inspect the vouchers if he went to the offices of the Institute.

This over, the PRESIDENT referred to the labours of the retiring secretary, Mr. Charles E. Groves, F.R.S., and particularly to those of the last two years, and informed the meeting that the council had voted an honorarium of 100 guineas to Mr. Groves on his retirement. He also took this opportunity to introduce the new secretary, Mr. G. H. Robertson. Then came the President's Address, which was a vigorous defence of the professorial, as distinguished from the professional, element on the council. The "opposition" had made much of this preponderating influence; but its influence in numbers was reduced to actual facts very neatly by the Presidential remarks, whilst its influence as an "elevator" of professional efficiency was made much of.

The attempt at defining a professional chemist was dexterously put when Dr. TILDEN asked whether he was or was not the professor who trained and often gave advice in "consultation"; the "works" chemist, whose importance he magnified; or the analyst, who in luxurious reception-rooms gave advice, and who also did "water analyses" at 7s. 6d. a piece, or "carbon determination in steel" at 9d. a determination.

The PRESIDENT then feelingly referred to the losses by death of Drs. Heisch and Henry, F.R.S. Among others Dr. Tilden spoke of Thomas Hyde Hills as a warm friend. The address was spiritedly delivered, and even when assent was not given applause was accorded.

Dr. FRANKLAND, F.R.S., proposed a vote of thanks to the President, and asked that the Address should be printed, and, commenting on it, remarked that while infallibility could not be claimed for the council, honesty and a sincere desire to promote the interests of the profession could. He illustrated the absurdity of one section only predominating by a recital of what befell his spectacles years ago in Germany. The frame was made of silver, but gilt. The doctor then took them to a goldsmith for repair; this worthy declined to undertake the

matter as they were not all gold. Not disturbed, the doctor handed them to a silversmith; he, observing that they were not all silver, refused to repair them. So, inferred the speaker, you cannot have your Institute without alloy. Both elements were good, and to refuse to work together was folly indeed. Dr. Frankland instanced the legal profession, in which there was now a strong movement in favour of fusion of the two branches; also the medical, in which, although there was a certain amount of differentiation, yet there was a very considerable amount of unanimity.

Mr. William Thomson, of Manchester, the secretary of the association formed to promote united action among the opposition, supported Dr. Frankland's motion, and for himself and party disclaimed any intention or desire to attack the President or the Professor individually.

Mr. Cassall, the opposition leader in the late council, also disclaimed, and professed his desire to keep the professors, but to get a more proportionate representation of the various classes of the profession. The motion was carried enthusiastically.

The report of the council was the next business, and after a small "wrangle" it was agreed to be taken "as read"; but remembering that the "closure" had been put upon further discussion on some previous occasion, the opposition, represented this time by Mr. Otto Hehner, the President of the Society of Public Analysts, moved to omit certain words in the report, and insert others, respecting the presentation of the scheme of examination for Fellows to the members before actual adoption.

Mr. Hehner gave an important warning against stifling discussion, and urged that the Annual Meeting was the time, almost the only time, the members had of submitting their views to the council.

Mr. Kingzett supported this view in trenchant terms.

Mr. Friswell opposed it.

Dr. Smith drew attention to the fact that the report was that of the council, and should either be received or rejected.

Seeing danger, Mr. Tyrer reminded the President (who, by the way, had never been present at an Annual Meeting before) that one of his predecessors had ruled any amendment out of order, and, after the report had been accepted, ruled discussion thereupon, or upon questions relating to the policy of the council, also out of order; and concluded by asking the President whether he intended to adopt that unhappy precedent.

The President at once ruled that no amendment could be moved on the report of council, but gave the assurance that opportunity for free and full discussion should be given.

Scrutineers were next appointed, and voting proceeded. The names of nine censors nominated were put on the blackboard, and a ballot taken for four. The new secretary and Mr. Tyrer acted as counters. The censors are officers whose duty it is to investigate charges of unprofessional conduct of the part of the Fellows. Drs. Bell and Frankland and Prof. T. E. Thorpe came out highest, with Messrs. Cassall and Howard next with a tie, which the President untied, in accordance with the bye-laws, by giving a casting vote to Mr. Cassall, the opposition candidate,—a proceeding which brought down the house. The work of the scrutineers appeared likely to be lengthy, so a welcome adjournment for an hour and a half took place. In due time (nearly ten by the clock) the meeting resumed; but the results had leaked out beforehand, and there was considerable excitement as to what course the President would take. It must be first explained that many times during the evening had the legality of particular acts of the council and of persons been challenged, chiefly because of an ambiguity in the charter and the bye-laws in regard to "arrears." In the article of the charter relating to voting for the council it is specifically stated that no one in arrear on January 1, prior, &c., shall be eligible to vote; while immediately afterwards the word is used in relation to the rights of membership, which cannot be taken away until the member has been twelve months in "arrear." It was well known that "arrears" had been tendered in the room, and the interest grew intense when Mr. Thomson, one of the scrutineers, rose to state that by direction of the secretary, Mr. Groves, they had "set aside" unopened 150 voters' envelopes, on the ground that the subscriptions of these voters had not been paid. Mr. Hehner used emphatic language. Mr. Cassall implored the President to act, in the presence of grave doubt, on former precedents, viz., to disregard the arrears in the limited sense, and to view the right to vote in the broad sense of a member's privilege.

The President, who kept quite cool, ruled that he had no choice but to decide that no vote of a member in arrear could be admitted; but, since among the opened papers there were admittedly those of members who had paid since January 1, he would accept the proposal for an adjournment of the meeting to Friday, March 11, when the same scrutineers would revise the unopened envelopes, and then reject the votes of those whose subscriptions were not then received. The new secretary was instructed to notify every member of the Institute of the adjourned meeting, and each of the 150 in arrear of subscriptions to pay up.

The formal motion for adjournment was made, and Mr. Hehner proposed, at 10.45 p.m., a vote of thanks to Dr. Tilden for his urbanity, courtesy, and tact, which was well deserved and we may say "earned."

Adjourned General Meeting.

At the adjourned Annual General Meeting held on Friday, March 11th, Mr. Markly, the solicitor who has acted for the Society, was present. Proceedings opened by the President reading the opinion of counsel, which had been obtained relative to the right of members to vote who had not paid their annual subscription. The opinion was to the effect that all members might sign and return a balloting list, but that any member who had not paid his subscription was not entitled to vote on any motion.

After some discussion as to whether marks or comments invalidated voting lists, the President ruled, after consultation with the solicitor, that only those papers were invalid which contained more than the proper number of names, or which for any other reason produced an ambiguity in the minds of the scrutineers as to the intention of the voter.

The scrutineers were now dismissed to complete the task left incomplete through the rejection of the 150 voting lists. On their return they announced that the official list was duly elected.

President—W. A. Tilden, D.Sc., F.R.S., &c.

Vice-Presidents—J. Bell, C.B., Ph.D., D.Sc., F.R.S., &c., M. Carteighe, F.C.S., E. Frankland, D.C.L., F.R.S., &c., Charles E. Groves, F.R.S., &c., W. Ramsay, Ph.D., F.R.S., &c., J. Emerson Reynolds, M.D., F.R.S.

Treasurer—David Howard, F.C.S.

Ordinary Members of Council—M. A. Adams, F.C.S., A. H. Allen, F.C.S., F. Clowes, D.Sc., F.C.S., A. Dupré, Ph.D., F.R.S., &c., R. J. Friswell, F.C.S., A. J. Greenaway, F.C.S., H. J. Helm, F.C.S., D. B. Hewitt, M.D., F.C.S., &c., J. F. Hogdes, M.D., F.C.S., J. Hughes, F.C.S., E. Kinch, F.C.S., G. H. Makins, F.C.S., R. Meldola, F.R.S., &c., O. Hehner, F.C.S., H. F. Morley, M.A., D.Sc., F.C.S., F. J. M. Page, B.Sc., F.C.S., &c., R. T. Plimpton, Ph.D., F.C.S., A. Smithells, B.Sc., F.C.S., J. C. Stevenson, M.P., F.C.S., C. O'Sullivan, F.C.S., F. L. Teed, D.Sc., F.C.S., J. Millar Thomson, F.C.S., W. Thorp, B.Sc., F.C.S., T. E. Thorpe, Ph.D., F.R.S., &c., T. Tyrer, F.C.S., E. W. Voelcker, Assoc.-R.S.M., C. R. A. Wright, D.Sc., F.R.S., &c.

The Presence of Mannite and Sorbite in the Fruits of the Cherry-Laurel.—Camile Vincent and Delachanal.—These two compounds are present in equal proportions in the fruits of the cherry laurel.—*Comptes Rendus.*

NOTICES OF BOOKS.

The Foundations of Chemistry. ("Grundlagen der Chemie.") By D. Mendeleeff. Translated from the Russian by L. Jawein and A. Thillot. St. Petersburg: Ricker.

We have here the eighth and concluding issue of the German version of Prof. Mendeleeff's great work. It embraces the platinum metals, as also silver and gold.

No generalisations are appended; but, *apropos* of the researches of Stas on the atomic weight of silver, there is a critique of Prout's hypothesis, in which is reproduced an extract from the address delivered by the author before the Chemical Society of London, in 1889. To this oration we need the less refer as it is in the hands of every reader of the Chemical News.

Of the work as now completed, if we leave on one side its very pronounced hostility to the doctrine of elemental evolution, it is scarcely possible to speak too highly.

Zeitschrift für Anorganische Chemie. Vol. I., Part 1. Edited by Gerhard Krüss (of Münich). Hamburg and Leipzig: Leopold Voss.

This new journal, exclusively devoted to inorganic chemistry, makes its appearance in a manner which augurs well for its future success.

The principal papers in its first number are an investigation of phosphoroxysulphide, by T. E. Thorpe and A. E. Tutton.

This compound is obtained on heating together phosphorous anhydride and sulphur in an atmosphere of carbon dioxide or nitrogen. The reaction sets in at 160°, and the mixture solidifies without any development of gas. The result is an addition product of the composition $P_4O_6S_4$. On sublimation *in vacuo* it is obtained in crystals. If the quantities of the ingredients employed are too large (exceeding 3 to 5 grms. phosphortrioxide), a violent explosion may ensue. The compound melts at 102°, and boils at 295°. It deliquesces in the air, giving off an odour of sulphuretted hydrogen. It is readily soluble in double its volume of carbon disulphide, from which it crystallises out unchanged.

"On the Double Acids of Septatomic Iodine," C. W. Blomstrand.—This comprehensive paper discusses the so-called double or complex acids, but it does not admit of useful abstraction.

"Action of Hydrogen Peroxide upon some Fluorides and Oxyfluorides," A. Piccini.—The author, on April 5th, 1891, submitted to the Accademia dei Lincei a memoir on the action of hydrogen peroxide upon normal potassium fluoxymolybdate, in which he described the compound $MoO_3F_2 2KFH_2O$. He also described a compound which he obtained on treating potassium fluoxytungstate with hydrogen peroxide. He describes now rubidium and cæsium fluoxypermolybdates and a triammoniumfluoxypermolybdate.

"On some Ammoniacal Platinum Compounds," Oscar Carlgren and P. T. Cleve.—The authors have studied the behaviour of sulphurous acid upon platinum iodonitrate, and that of hydrogen peroxide upon the platodiamine salts.

"The Production of Tungstates Free from Molybdates," Carl Friedheim and Rich. Meyer.—The authors prepare a saturated solution of ordinary sodium tungstate in cold water, and add in the cold hydrochloric acid until the solution is feebly alkaline. The paratungstate which crystallises out is re-crystallised once, by which the proportion of molybdenum in the product is reduced by four-fifths. Half of the salt present is decomposed by hydrochloric acid and a little nitric acid in a boiling solution, and the fine yellow hydrated tungstic acid obtained is thoroughly washed with hot water. It is then well stirred up with water and added in the smallest possible quantities to the boiling solution of the other half of the salt until a specimen is no longer precipitated by an addition of hydrochloric acid. After adding a little hydrochloric acid to the filtered solution, it is heated to ebullition and repeatedly precipitated by means of sulphuretted hydrogen; the filtrate is concentrated (when a little more sulphide separates out), the blue solution is oxidised with a few drops of bromine water, and neutralised with sodium hydroxide, when the pure paratungstate is obtained on crystallisation.

The presence of molybdenum in tungstic acid and the tungstates appears to have been hitherto overlooked and raises the question whether the atomic weight of tungstate has been accurately determined.

The list of chemists who co-operate in the new journal contains the most eminent names in inorganic chemistry in all countries in which science is diligently cultivated. The list of papers that have been sent in for the succeeding numbers is such that they will without doubt be eagerly anticipated.

Instructions for the Use of Hunter and Driffield's Actinograph. (Patented). Entered at Stationers' Hall. London: Marion and Co.

The instrument described in this pamphlet will probably be of great service to photographers; though whether its name has been happily selected is a question into which we need not enter. It is not, as a reader might possibly expect, an apparatus for taking an observation of the intensity of the light and recording the results. It seems, on the contrary, merely to supply data for calculating what the light ought to be. The authors admit that "many photographers would prefer an actinometer or direct means of measuring the light;" but they consider the actinograph preferable, because from it "the condition of the light may be ascertained at the precise moment of making the exposure;" whilst an actinometer "gives the condition of the light some time previously."

The instrument in question consists of four scales, expressing respectively the light, the lens, the exposure, and the speed of the plate. The amount of light is shown by a revolving scale for every day of the year, and for every hour of the day when it is photographically active. It is assumed that, apart from atmospheric influence, the amount of light is "merely a function of the sun's altitude A short sliding scale is to take account of the greater or less transparency of the atmosphere. It is marked with the words "very light," "bright," "mean," "dull," and "very dull;" and we are told that "the exposure must be selected opposite that point which most nearly corresponds with the atmospheric conditions at the time of exposure. A "mean" light is defined as being when there is "just sufficient sun to cast a very faint shadow," and very dull is to indicate the dullest light in which it would be at all reasonable to take a photograph.

Above this is a longer movable slide indicating the time in seconds from 0·05 to 60.

At the bottom is a slip marked with figures indicating the speed of plate.

The pamphlet contains very full instructions for the use of the instrument, accompanied with examples. It is remarked that each particular actinograph is adapted only for a certain range of latitude.

On Stereochemistry and the Laws of the Rotatory Power.—Ph. Guye.—A reply to two memoirs by M. Colson (*Comptes Rendus*, cxiv., pp. 175 and 417). If we do not admit the reality of the formulæ, such as CH_3,CO,O and CO,O,CH_3, it is not possible to constitute stereochemistry. The chemical notation does not exclude molecular combination. Nothing in the theories of Le Bel and Van 't Hoff permits us to affirm that their notation implies that all the derivatives of a dextrorotatory body must be dextrorotatory.—*Comptes Rendus.*

OBITUARY.

THE LATE Dr. C. MEYMOTT TIDY.

Sanitary and forensic chemistry have sustained a heavy and unexpected blow by the death of Dr. C. M. Tidy, which took place on Tuesday, March 15. Upon sanitary questions, especially with reference to water supply and river pollution, the deceased chemist took a prominent position. Not only was his knowledge profound, but it was ready at command. He was unrivalled in seizing at once upon the salient points of any question, and in devising experiments to test the accuracy of the arguments and theories adduced, whether by colleagues or opponents. In addition to these qualifications, he possessed in an eminent degree the *uncommon* faculty known as "common sense." Hence, Government Departments, Parliamentary Committees, Law Courts, and Municipalities accorded to his evidence and his opinions an almost unlimited weight. His papers read before the Society of Arts and his lectures delivered to the students at Lincoln's Inn were exceedingly valuable. Here, as on all other occasions, he was distinguished for his adroitness in tearing to pieces unfounded theories and exposing the hollowness of sensational schemes for the water supply of the metropolis. In conjunction with Mr. Crookes and Prof. Odling he had carried on for years a searching inquiry into the quality of the London waters, and had done much to dispel the scare which had been industriously created concerning the quantity of impurities said to be swallowed yearly by the people of London in the shape of water.

Dr. Tidy's principal works, in addition to the reports on the London water supply elaborated in conjunction with Mr. Crookes and Prof. Odling, are his "Handbook of Modern Chemistry" (1878); "Handy Book of Forensic Medicine and Toxicology," 1877 (in conjunction with W. B. Woodman); "Legal Medicine," 1883.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—The Annual Meeting of the Institute has come and gone, and although the "House List" has been elected as the new Council, the results of the polling show that I was mistaken when I supposed that the opposition had comparatively few sympathisers. When one makes a mistake it is one's duty frankly to own it.

If, as in the present case, about one-third of the members of the Institute range themselves under the banner of the dissatisfied, it seems only fair and just that the newly elected Council, which presumably represents the majority, should as soon as possible take steps to ascertain the causes of dissatisfaction, and the wants of the members at large. Although, in the ordinary nature of things, it is impossible that all the former can be removed or all the latter can be supplied, much can no doubt be done to improve the present state of affairs.

This contested election will probably do good if both sides agree to work heartily together for the common weal, but if the body of members becomes split up, divided into parties and factions, it will certainly retard our progress towards the attainment of the end which the founders of the Institute had in view, namely, that of raising our profession so that it may ultimately take rank with the learned professions.—I am, &c.,

Charles E. Groves.

Guy's Hospital, March 14, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 9, February 29, 1892.

New Researches on the Monohaloidic and Monocyanic Aceto-acetic Ethers.—A. Haller and A. Held.—This paper is not suitable for useful abstraction.

Temperatures Developed in Industrial Furnaces—H. Le Chatelier.—The author takes as points of comparison the melting-points determined by M. Violle, viz., sulphur 448°, gold 1045°, palladium 1500°, platinum 1775°. He finds the melting-heat of white cast-iron 1135°, and that of grey cast-iron 1220°. Mild steel melts at 1475°, semi-mild at 1455°, and hard steel at 1410°. The furnace for hard porcelain at the end of the baking has a heat of 1370°. The heat of a normal incandescence lamp is 1800°, but it may be pushed to beyond 2100°. Previous determinations have been falsified by using for comparison the melting-points of palladium and platinum. Thus the temperature of the Bessemer process was fixed by Langley at 2000°, because platinum seemed to melt rapidly in the flame. It does not really melt, but it merely dissolves in the minute drops of melted steel carried along by the gaseous current.

A Series of New Compounds—Chromosulphuric Acid and the Metallic Chromosulphates.—A. Recoura.—This paper will be inserted in full.

Researches on the Application of the Measurement of Rotatory Power to the Determination of the Compounds formed by the Aqueous Solutions of Perseite with Sodium and Ammonium Molybdates.—D. Gernez.—The rotation of the aqueous solution which is $-0° 11'$, becomes positive on the addition of a quantity of salt which represents about 1-150th of the molecular weight of the molybdate. It increases by equal quantities if we add to the same volume equal quantities of salt, which leads us to admit that for each of these weights there takes place a combination with corresponding weights of perseite. The rotation which increases very regularly until we have added a quarter of the molecular weight of the molybdate, reaches a maximum value for a quantity a little greater than $\frac{6{\cdot}75}{24}$ of the molecular weight. These proportions would correspond to combination of 1 mol. of perseite and 1·969 mols. of molybdic acid if we admit the formulæ—

$$C_7H_{16}O_7 \text{ and } 3Na_2O.7MoO_3.11H_2O,$$

—representing respectively the composition of perseite and of acid sodium molybdate. But on examining closely the results of the experiment, it appears that for 2 mols. of molybdic acid the weight of salt corresponding would be $\frac{6{\cdot}857}{24}$ of the molecular weight; but for the addition of this quantity of salt the rotation observed, $7° 5'$, is inferior to the rotation which corresponds to $\frac{6{\cdot}75}{24}$. We may, however, interpret these results, as the author has done in case of mannite and of sorbite, remarking that whilst molybdic acid alone has a very decided action upon perseite, acid sodium molybdate does not at all affect its rotatory power. We are thus led to infer that acid sodium molybdate acts by the excess of molybdic acid which it contains. Beyond the maximum the rotation gradually decreases, which indicates that there is a dissociation of the compound previously formed and a tendency towards new equilibria. The results of experiments made with perseite and acid ammonium molybdate lead to identical conclusions.

Action of Soda and Potassium Cyanide upon Chlorodiamylamine.—A. Berg.—The reaction of alcoholic soda upon chlorodiamylamine leads to the formation of amylamylidenamine—

$$\begin{matrix} C_5H_{11} \\ C_5H_{10} \end{matrix} \!\!> N.$$

The product of the reaction of potassium cyanide is diamylcyanamide—

$$\begin{matrix} C_5H_{11} \\ C_5H_{11} \\ CN \end{matrix} \!\!> N.$$

If treated with hydrychloric acid at 160° it is split up into carbonic acid, ammonia, and diamylamine.

On Metaphenyltoluene.—G. Perrier.—Of the three isomeric phenyltoluenes which theory foresees, the ortho has been studied by Barbier, and the para by Carnelley and Thomson. The author has obtained the meta-compound by causing an excess of sodium to react upon a mixture of equal mols. of metabromtoluene and of phenyl bromide dissolved in anhydrous ether, and heated for about 105 hours in a reflux apparatus to between 40° and 50°. The liquid is freed from ether and submitted to distillation. The product passing over between 245° and 275° is collected. It consists of diphenyl and the new hydrocarbon. It is submitted to the action of a mixture of ice and snow, when the chief part of the diphenyl crystallises. After a series of distillations followed by refrigerations with methyl chloride, a liquid is obtained, which, after distillation over sodium, did not combine with Fritzsche's reagent, and had the constant boiling-point 270°, and the composition $C_{14}H_{12}O_7$.

The Formation Heats of the Potassium Carballylates.—G. Massol.—A thermo-chemical paper, not admitting of useful abstraction.

Specific Gravity of Textile Fibres.—M. de Chardonnet.—The author considers that Leo Vignon's method does not give the true density of the fibres, because the occluded air is not completely eliminated. The results given by Leo Vignon are too low; for cotton he gives the figure 1·50 instead of 1·95; for wool 1·30 instead of 1·61.

Detection of Resin Oil in Oil of Turpentine.—M. Zune.—If the latter oil is pure the difference between the index of the first quarter of the distillate and that of the last quarter should not exceed 400 units of the fifth decimal place, and will be almost always below 350. The presence of even one per cent will raise it to more than 600 units.

Comparative Nitrification of Humus and of Unaltered Organic Matter, and Influence of the Proportions of Humus upon Nitrification.—P. Pichard.—The use of marl is much preferable to that of lime on account of its property of retaining ammonia, of fixing the atmospheric nitrogen more abundantly.

Medical Utilisation of Alternating Currents of a High Potential.—G. Gautier and J. Larat.—The ozone produced by electric discharges is, in fact, largely mixed with nitrous products. The gas seems to a certain extent poisonous, as it readily occasions vertigo, angina, and even bronchitis.

The Composition of Hæmocyanine.—A. B. Griffiths.—Hæmocyanine may be precipitated from the blood of *Homarus*, *Cancer*, and *Sepia*, by magnesium sulphate. The precipitate is dissolved in water and re-precipitated by alcohol. Its composition is $C_{867}H_{1303}N_{223}CuS_4O_{258}$. Hæmocyanine has a very uniform composition, differing in this respect from hæmoglobine. It is also much more stable.

The Ptomaines in Some Infectious Diseases.—A. B. Griffiths.—The method pursued by the author for extracting the urinary ptomaines has been already described in the *Comptes Rendus*, vol. xciii., p. 656. 1. *Measles.*—The ptomaine extracted from the urine of the patients is a white, crystalline substance, soluble in water, with an alkaline reaction. Its chloroplatinate forms microscopic crystalline needles. Mercuric chloride yields a double salt, almost insoluble in water, which crystallises in prismatic needles. This ptomaine is also precipitated by the picric, phosphomolybdic, and phosphotungstic acids. Its composition is expressed by the formula $C_5H_5N_3O$. It is very poisonous. 2. The ptomaine obtained from the urine in cases of whooping-cough is white, crystalline, and soluble in water. It forms a hydrochlorate and a chloraurate, it gives a white precipitate with phosphomolybdic acid, a yellow precipitate with picric acid, and a maroon precipitate with tannin. Its composition is $C_5H_{10}NO_2$. Afanassieff's bacillus found in matter expectorated in whooping-cough has the same composition. Neither of the two ptomaines described above is found in normal urine.

MISCELLANEOUS.

Crystal Palace Electrical Exhibition.—The following gentlemen have kindly consented to serve on the jury for this Exhibition:—Prof. W. Grylls Adams, D.Sc., F.R.S., Prof. W. E. Ayrton, F.R.S., Mr. Shelford Bidwell, M.A., F.R.S., Mr. Conrad Cooke, M.Inst.E.E., Prof. W. Crookes, F.R.S., Mr. W. B. Esson, M.Inst.E.E., Major-Gen. Festing, R.E., F.R.S., Prof. George Forbes, M.A., F.R.S., Capt. Sir Douglas Galton, K.C.B., D.C.L., F.R.S., Dr. J. H. Gladstone, F.R.S., Mr. J. H. Greathead, M.Inst.C.E., Mr. Charles Hall, M.Inst.E.E., Prof. D. E. Hughes, F.R.S., Sir Henry Mance, C.I.E., Mr. W. H. Massey, M.Inst.C.E., Mr. W. H. Preece, F.R.S., Mr. A. Reckenzaun, Prof. Henry Robinson, M.Inst.C.E., Capt. Sankey, R.E., M.Inst.E.E., Mr. C. E. P. Spagnoletti, M.Inst.C.E., Mr. James Swinburne, M.Inst.E.E., Prof. Silvanus Thompson, D.Sc., F.R.S., Mr. J. Tomlinson, M.Inst.C.E., Prof. W. C. Unwin, B.Sc., M.Inst.C.E., Major-General Webber, C.B., R.E., Mr. J. W. Wilson, M.Inst.C.E.

MEETINGS FOR THE WEEK.

MONDAY, 21st.—Medical, 8.30.
—— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).
TUESDAY, 22nd.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8. Exhibition of Old Silver Prints. Mr. Dallmeyer will show his Telephotographic Lens. "On Copying Inclined Pictures," by Mr. Chapman Jones.
WEDNESDAY, 23rd.—Society of Arts, 8. "Manufacture and Industrial Application of Flexible Tubing," by Gilbert R. Redgrave.
—— Geological, 8.
THURSDAY, 24th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Epidemic Waves," by B. Arthur Whitelegge, M.D., B.Sc.
—— Society of Arts, 8. "The Opium Question," by G. H. M. Batten.
FRIDAY, 25th.—Royal Institution, 9. "Posy Rings," by John Evans, D.C.L., LL.D., &c.
—— Physical, 5. "Electromotive Forces of Gold and Platinum Cells," by Prof. Herroun. On a New Instrument for Showing the Effects of Persistence of Vision," by E. S. Bruce, M.A. "Some Electrical Instruments," by R. W. Paul.
SATURDAY, 26th.—Royal Institution, 3. "Dramatic Music, from Shakspeare to Dryden," by Prof. J. F. Bridge, Mus. Doc.

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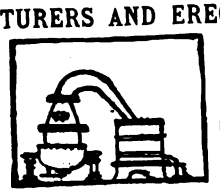

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Vol. LXV., No. 1687.

CHANGES OF ELECTROMOTIVE FORCE, VOLUME, AND TEMPERATURE BY MIXING ELECTROLYTES.*

By Dr. G. GORE, F.R.S.

In a paper on "Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c., of Electrolytes" (*Philosophical Magazine*, August, 1891, p. 157), I have shown the effects of *dilution* upon the temperature and total volume of the liquids, and upon the *mean amount* of electromotive force of a voltaic couple immersed in them. In the present case, I have examined in a similar manner the effects of *mixing* electrolytes upon the same phenomena, and in order to obtain some new information respecting the chemical substitution of acids and the double decomposition of salts, I have employed pairs of what I venture to term "isomeric mixtures. The mixtures I employed were all of them dissolved in distilled water, and are divided into two groups, viz., 1st Section, acids + salts, for examining the substitution of acids; and 2nd, salts + salts, for examining double decomposition.

All the substances employed were taken in the proportions of their chemical equivalents, and in each case the equivalent weight in grains of each ingredient was dissolved in 1800 grains of water; and, after measuring their separate amounts of electromotive force, the two solutions were mixed, and the changes in their temperature, total volume, and *mean* amount of electromotive force ascertained; the quantity of each salt usually employed in a thermal measurement varied from 30 to 100 grains. A cadmium-platinum voltaic couple and a thermo-electric pile of german silver and iron were used for measuring, by the method of opposition, the changes of electromotive force at ordinary atmospheric temperature, and the measurements are given in volts. The thermometer employed was capable of measuring 0·01° C. Details of the mode of experimenting and of measuring the changes attending the act of mixing has already been given in the paper referred to, and in another one on "A Method of Measuring Loss of Energy Due to Chemical Union, &c." (see *Phil. Mag.*, Jan., 1892, p. 28).

A series of tables of isomeric mixtures of acids + salts are given in the full paper, showing changes of *mean* electromotive force, total volume, and temperature of 15 isomeric couples of mixed liquids, attending the expulsion of one acid from a salt by means of another.

A circumstance to be noticed in these tables is, that every mixture suffered a change either of total volume, temperature, or mean amount of electromotive force, or of all three, during the mixing; thus showing that with each pair of ingredients either a chemical or a molecular change had occurred. And another fact to be observed is that in every instance each of the two mixtures of an isomeric couple gave the same amount of electromotive force. From the latter we may conclude that, in the entire fifteen cases, each of the two pairs of ingredients formed the same final product during the mixing; the two started with different amounts of energy, but both arrived at the same final condition.

The difference of behaviour, both as regards change of electromotive force, of total volume, and of temperature between the two mixtures of an isomeric couple is, in nearly every instance of the series, quite manifest; in nearly all cases, the one mixture gives a greater gain of electromotive force than the other; and the one gives an increase and the other a decrease of temperature; and, in most cases the one gives a contraction and the other an expansion of volume; the one which gave the smallest gain of electromotive force usually also gave the greatest contraction of volume. Out of the thirty mixtures, twenty-nine gave a gain, and one gave a loss of electromotive force; this proportion would differ with each different positive metal used in the voltaic couple. (See "A Method of Measuring Loss of Energy Due to Chemical Union, &c., of Electrolytes," *Phil. Mag.*, Jan., 1892, p. 28).

All change is relative, if we view the numbers not as actual amounts of opposite kinds of action, but only as relative ones of the same kind, *i.e.*, each loss of electromotive force as being only a smaller gain, each contraction of volume as only a smaller expansion, and each increase of temperature as only a smaller decrease; the three series of changes are found to agree with each other in thirty-three out of the forty-five possible ways of comparing them. Thus, the largest gain of *mean* electromotive force is attended by the greatest expansion of volume (and increased freedom of molecular motion) in nine cases, and by the largest decrease of temperature (and absorption of heat) in fourteen cases, and the largest expansion of volume is accompanied by the greatest decrease of temperature in ten cases. The connection between *mean* electromotive force, mean specific gravity, and latent heat is thus distinctly shown, and more clearly than in cases of simple dilution of acids and salts by water in a previous research (see "Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c., of Electrolytes," *Phil. Mag.*, Aug., 1891, p. 157). Some of the exceptional cases may probably be explained by assuming that one liquid of one mixture dilutes the other one, and thus allows greater freedom of molecular motion, which more than compensates larger contraction of volume or greater loss of heat.

With regard to the relative degrees of energy of chemical action in the two mixtures of each isomeric couple, the tables supply three different kinds of evidence, viz., change of volume, of temperature, and of *mean* electromotive force; and, in accordance with well-known general truths in chemistry, we may infer that the compound which during the act of mixing gives the largest proportion of contraction (or smallest expansion) of volume, the largest evolution (or smallest absorption) of heat, and the greatest loss (or smallest gain) of mean electromotive force is probably the one in which chemical union is the strongest. In each of the fifteen instances of isomeric couples, the mixture in which the strongest molecular and chemical union is supposed, according to this view, to occur is placed the first.

With regard also to the question of chemical substitution of one acid by another, and which of two acids is the strongest whilst in a state of solution, if the relative degree of strength of chemical action are truly though only approximately represented by the amounts of contraction of volume, of evolved heat, and decrease of mean electromotive force, we may infer that, in the examples given, sulphuric acid has a greater power of expelling nitric acid than nitric has of expelling sulphuric, that it has greater power of expelling hydrochloric acid than the reverse, and of expelling acetic acid than the reverse; that hydrochloric acid has greater power of expelling nitric acid than the opposite, and that hydrochloric acid has greater power of expelling hydrobromic acid than the reverse. With regard to the couple No. 4, however, according to J. Thomsen, "when soda, nitric acid, and sulphuric acid mutually react in equivalent quantities in a dilute solution, two-thirds of the soda combines with the nitric acid, and one-third with the sulphuric acid," and "nitric acid in aqueous solution is a stronger acid than sulphuric" ("Principles of Chemistry," by P. Muir, p. 437); according to Ostwald, also, the strongest acid is

* Abstract prepared by the Author of a Paper read before the Birmingham Philosophical Society, and recently published in vol. viii., Part 1, p. 23 of the *Proceedings* of the Society.

the one which takes the largest proportion of base ("Outlines of General Chemistry," translated by J. Walker, p. 324). When this couple, in very dilute solutions, was examined by the voltaic balance method, the mixture $H_2SO_4 + 2NaNO_3$, during the mixing at once changed to the final state; whilst the other one, $2HNO_3 + Na_2SO_4$, required the assistance of heat, as if the action of the sulphuric acid was stronger than that of the nitric (see *Phil. Mag.*, Oct., 1889, p. 290). The most fundamental question, however, is probably not what are the relative strengths of different acids, but what are the relative directions and velocities of the molecular motions of the substances?

In the next section (B), mixtures of salts with salts were similarly examined. In this case, the magnitudes of nearly all the changes were much smaller than in Section A, salts + acids. Each of the twenty mixtures, however, showed an alteration either of mean electromotive force, total volume, or temperature due to the act of mixing; thus indicating the occurrence of either a molecular or a chemical change in every instance.

In each of the ten isomeric couples examined, the amount of electromotive force produced by each of the two mixtures was the same, thus indicating that they had both passed to the same final state and attained the same molecular or chemical composition.

The much larger proportion of cases of loss to those of gain of mean electromotive force in this section than in Section A was no doubt due to the employment of salts + salts instead of acids + salts. A similar result was obtained in a previous research, in which isomeric mixtures were not used (see "A Method of Measuring Loss of Energy during the Chemical Union, &c., of Electrolytes," *Phil. Mag.*, Jan., 1892, p. 28).

The three series of changes of volume, temperature, and electromotive force in this section largely agree with each other, but the agreement is generally less distinct than with the series of mixtures of acids + salts.

General Remarks.

The results obtained in this research, and in the one on "A Method of Measuring Loss of Energy during Chemical Union, &c., of Electrolytes" (*Phil. Mag.*, Jan., 1892), show that when one electrolyte is added to another each electrolyte so affects the other during the act of mixing that the total volume, the mean amounts of latent heat and of electromotive force (and probably of other properties of the liquids, such as refractive power, transparency to various kinds of radiant energy, &c.) of each of the two substances are altered. Similar changes of volume and of temperature are already known.

The fact that the three classes of results obtained in this research extensively agree with each other indicates that they are connected with some very fundamental property of matter; whilst the absence of apparent agreement between them in a minority of cases is probably due to some minor circumstance. The lack of perfect agreement between the three different classes of effects, both with acids + salts and with salts + salts, shows that the phenomena are less simple than at first sight they appear to be. As the molecules of all substances are in a ceaseless state of motion, it is probable that the alterations of volume, temperature, and electromotive force are results of changes of amount of opposite motions of the molecules of the two mixed substances. According to this view, the loss of heat and the production of chemical and voltaic action are due to neutralisation and other changes of molecular motion.

If the changes of volume, temperature, electromotive force, and total molecular energy are results of neutralisation of opposite or incompatible motions of the two substances, we may infer that in a case of chemical union the molecular motion of the constituent A of a mixture of electrolytes so alters that of the one B, and the latter so affects that of the former during the act of mixing, a usually to decrease the total volume, the latent heat, the mean amount of that portion of the molecular motion of each dissolved electronegative substance which is incompatible with the molecular motion of the positive metal; and consequently, also, the mean amount of electromotive force. The results obtained by experiment in this research, and in the one referred to (*ibid.*), show that if A is an acid and B is a base, the total volume, the latent heat, and the mean amount of electromotive force are usually largely *decreased*. If A and B are both salts, these effects are usually feeble and variable. If A is an acid and B is a salt, those effects are usually *increased* in one mixture of an isomeric couple and *decreased* in the other. And if A is a halogen and B is a salt, the *increase* in one mixture of such a couple is frequently greater, but if heat is then applied a large decrease usually occurs (*ibid.*).

These effects may be largely explained by the opposite influences of chemical union and dilution upon the degree of freedom of molecular motion, and, consequently, upon the electromotive force; *chemical union usually decreases and dilution usually increases the mean amount of electromotive force;* but the former produces a greater and more profound change than the latter. In nineteen cases out of twenty, the dilution of an acid or a salt solution by water was attended by an increase of mean amount of electromotive force (see "Relations of Volta Electromotive Force to Latent Heat, Specific Gravity, &c., of Electrolytes," *Phil. Mag.*, Aug., 1891, p. 157; also "A Relation of Electromotive Force to Equivalent Volume and Molecular Distance of Substances," *Proc. Birm. Phil. Soc.*, 1892, vol. viii., Part 1), as if the substances were in some degree "dissociated," or had acquired a greater degree of freedom of molecular motion; the latter appears the most likely. Similarly, when the ingredients of two different solutions which were mixed did not chemically unite, but their solutions merely diluted each other, the increase of *mean* electromotive force was greater (or the loss of it was less) in proportion as the degree of intimacy of union was less, and the uncombined or feebly combined electronegative substance had greater molecular and chemical energy; thus, in the case of addition of an acid to a salt, there was often a gain of *mean* electromotive force, because there was practically a dilution and an increased freedom of molecular motion of the acid unattended by chemical union; and if a halogen, instead of an acid, was used the gain was still greater, provided no chemical union occurred (see "A Method of Measuring Loss of Energy by Chemical Union, &c., of Electrolytes," *Phil. Mag.*, Jan., 1892). If, however, an acid solution was added to one of a base, there was usually a large loss of *mean* electromotive force, because there was chemical union, contraction of volume, loss of heat, and diminished freedom of molecular motion (*ibid.*).

The fundamental conditions of the phenomena are relative velocity and direction of molecular motion. The greater the velocity of the molecules of the electronegative constituent of the liquid, the greater usually is the electromotive force; thus, the halogens have greater molecular velocity, and produce a greater effect than acids, and acids than salts, and act more strongly upon the electropositive metal. The more opposite also in direction or incompatible the molecular motion of the electronegative constituent of the liquid, after mixing, is to that of the positive metal, the greater usually is the electromotive force; and the more opposite the molecular motions of an acid are to those of a base, the larger usually is the loss of energy and loss of *mean* amount of electromotive force during the union of those substances.

Relative degree of freedom of molecular motion, by influencing the molecular velocity has great effect, thus:—1. Diluting an acid or saline solution with water usually produces an increase of *mean* amount of electromotive force, especially with strong acids; actual trial gave nineteen out of twenty cases (see "Relation of Volta Electromotive

Force to Latent Heat, Specific Gravity, &c., of Electrolytes," *Phil. Mag.*, Aug., 1891, p. 157); 2. Add a solution of a salt to one of a salt, and there is but little gain of *mean* electromotive force, because the electronegative constituents of the salts, being chemically united to their respective bases, have but little freedom of molecular motion, and the effect of dilution of one liquid by the other is therefore small; 3. Add a solution of an acid to one of a salt, and both the *mean* electromotive force and the *gain* of mean amount of that force are larger, because free acid possessing greater velocity of molecular motion is present and dilution of one liquid by the other increases that motion; 4. Add a dissolved halogen to a dissolved salt, and there is usually a still greater gain of electromotive force and of mean amount of that force, because a free halogen has usually greater velocity of molecular motion than a free acid. If, however, we heat this latter mixture, chemical union usually occurs, freedom of molecular motion is diminished, and there is a large decrease both of electromotive force and of mean amount of that force; 5. Add a solution of an acid to one of a base and there is a great loss of heat, attended by large decrease of velocity and freedom of molecular motion and of mean amount of electromotive force, which more than neutralises the increased freedom of motion caused by the dilution.

If we examine the influence of the action of an acid upon a base with regard to its subsequent action upon the positive metal, we find that the larger the amount of molecular motion of the acid incompatible with that of the base, and the larger the loss of such motion as heat during mixture, the smaller usually is the amount of residuary molecular motion incompatible with that of the positive metal, the greater usually is the *loss* of mean amount of electromotive force, and the smaller is the actual electromotive force.

According to the foregoing explanation, in cases of *gain* of mean electromotive force, the changes of molecular motion during mixing a pair of electrolytes are such that the proportion of energy of the electronegative constituent of the mixture which is opposed to, and incompatible with, that of the positive metal of the voltaic couple becomes larger, and in cases of *loss*, the reverse. It does not, however, necessarily follow from this that the *total amount* of molecular motion of the liquid, or of the electronegative substances dissolved in it, is always greater when the mean electromotive force is increased, because we know by experiment that in some exceptional cases the latter is greater after the two liquids have lost molecular motion in the form of heat than previously (*ibid.*). Some of the exceptional cases may probably be explained by the increase of mean electromotive force attending dilution.

Upon the basis of Newton's third law of motion, that action and reaction are always equal, we may in all cases conclude that the loss of energy in the form of heat during chemical union, and the absorption of heat during the mixture of any two electrolytic substances, is equally divided between them.

As the degree of volta electromotive force is a direct result of, and inseparably connected with, strength of chemical action of the electronegative constituent of the liquid upon the positive metal, the foregoing general remarks on the relations of molecular motion to electromotive force apply largely to the relations of such motion to chemical action of that constituent on that metal, and the measurements of electromotive force are, to a certain extent, therefore, also measurements of strength of chemical action.

The chief new truth disclosed by this research is the distinct connection between changes of total volume, total heat, molecular motion, and *mean amount* of electromotive force. All the results obtained in this research help to confirm the existence of a mechanical basis of voltaic and chemical action.

THE CHROMOSULPHATES.

By C. F. CROSS.

A RECENT notice of the investigations of A. Recoura (*Comptes Rendus*, cxiv., 477) upon the above salts, which are described as "a series of new compounds" (CHEM. NEWS, lxv., 137) has attracted my attention. The author appears to have overlooked some researches published ten years ago bearing on this subject ("The Reaction of Chromic Anhydride with Sulphuric Acid," by Cross and Higgin, *Chem. Soc. Journ.*, xli., 113), establishing as they do the existence of chromosulphates of very considerable stability. The compounds which we described were prepared by heating CrO_3 and $K_2Cr_2O_7$ with H_2SO_4 at a temperature approaching the boiling-point of the latter. There appears to be a complete reduction of the CrO_3 to Cr_2O_3 under these conditions, the sesquioxide reacting with the sulphuric acid to form acid sulphates, which separate as amorphous precipitates in the acid liquid. From the CrO_3 we obtained chromosulphate of a lavender colour, somewhat variable in composition, but approximating to the formula $4Cr_2O_3.6SO_3.7H_2SO_4$; from the potassium salt, green compounds, generally similar in composition to the above, but with a proportion of the Cr_2O_3 substituted by K_2O. The analyses of these compounds gave the following mean numbers:—

	From CrO_3.	From $K_2Cr_2O_7$.
Cr_2O_3	34·8	26·6
SO_3	58·2	59·3
H_2O	7·2	7·1
K_2O	—	6·9
	100·2	99·9

In both, the ratio of acid to base is greater than the normal, and from the conditions of their formation we must regard the H_2O as present in the form of H_2SO_4. The compounds obtained from CrO_3 lose nearly the whole of their SO_3 on ignition, but both groups of sulphates are very resistant to the action of alkalis. It is evident that these results may be taken with those of M. Recoura as showing that some exceptional relationship obtains between CrO_3 and H_2SO_4 through a very wide range of conditions.

The later investigations of M. Recoura appear to have satisfactorily elucidated this relationship under the condition of the solution of the reacting molecules in water, and at the same time they reopen the problem which we attacked from a purely empirical standpoint, viz., the conditions of molecular equilibrium obtaining between Cr_2O_3 and H_2SO_4 in presence of excess of the latter and at the temperature of its boiling point. M. Recoura's observations supply a working hypothesis, with which I shall be enabled to reinvestigate the anhydrosulphates above described with some promise of solving the problem in question.

4, New Court, London, E.C.
March 19, 1892.

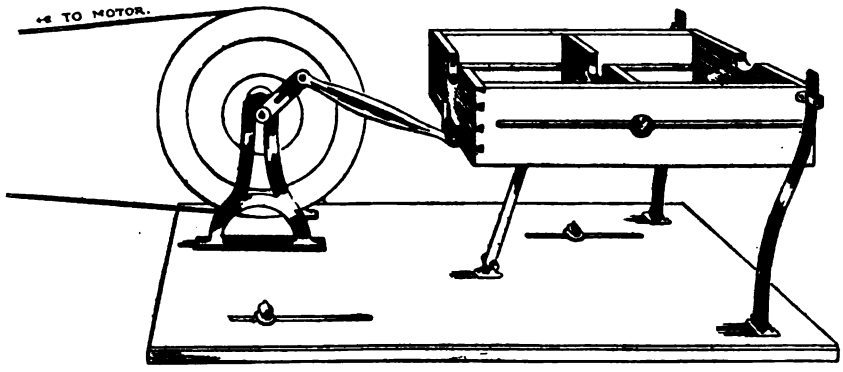
Royal Institution.—The following are the Lecture Arrangements after Easter:—Prof. T. G. Bonney, two lectures on "The Sculpturing of Britain—its Later Stages" (the Tyndall Lectures); Mr. Frederick E. Ives, two lectures on "Photography in the Colours of Nature"; Prof. R. C. Jebb, M.P., three lectures on "Some Aspects of Greek Poetry"; Prof. Dewar, four lectures on "The Chemistry of Gases"; Mr. R. G. Moulton, three lectures on "Faust"; Mr. E. Dannreuther, four lectures on J. S. Bach's "Chamber Music" (with many musical illustrations); Prof. H. Marshall Ward, three lectures on "Some Modern Discoveries in Agricultural and Forest Botany" (illustrated by lantern). The Friday Evening Meetings will be resumed on April 29th, when a discourse will be given by Dr. William Huggins on "The New Star in Auriga"; succeeding discourses will probably be given by Captain Abney, Dr. B. W. Richardson, Mr. J. Wilson Swan, Sir James Crichton-Browne, Mr. Ludwig Mond, Prof. Dewar, and other gentlemen.

ON A SIMPLE LABORATORY SHAKER.*

By WYNDHAM R. DUNSTAN and T. S. DYMOND.

In most laboratories, especially where research in organic chemistry is being carried on, the need for some mechanical arrangement for shaking is constantly felt. The extraction of solids with various liquids, the desiccation of organic liquids with a solid drying agent, the chemical action of a liquid on a substance not freely soluble in it, are a few out of many instances where time and trouble may be saved and greater efficiency secured by the employment of a mechanical contrivance for shaking. In the Research Laboratory of the Pharmaceutical Society such a machine, which works almost noiselessly, is now in constant use.

Having found that the arrangements for the purpose which are usually sold by apparatus-makers were unsuited to all our requirements, we devised a simple shaking machine, which in a form perfected by more than a year's experience, we now wish to bring under the notice of the Society. A very few words of explanation are necessary,



since the principle and mode of working of the shaker are readily apparent from the drawing.

It consists of a wooden truck into which can be firmly fixed, by means of a sliding partition, a bottle or other vessel of any size up to that of a Winchester quart. This truck is supported underneath, near the front, by a rod which is capable of moving backwards and forwards on a pivot. At the back, the truck is supported by two flexible steel laths, one end of each being clamped to either side of the truck, the other end being firmly fitted in the base-board of the machine. The necessary to and fro motion is communicated to the truck in the usual manner by means of a crank connected with a revolving wheel and joined to the truck by an iron or wooden rod. This rod can be attached to the crank at different distances from the axle, so that the extent of the excursions made by the truck may be varied. A cord from a water or other small motor passes over the wheel, which is grooved at three distances from the centre so that the rate of motion may be regulated. In order to avoid the necessity of altering the length of the cord which passes from the motor to the wheel, the base-board of the apparatus is provided with slots and thumbscrews by means of which it may be securely fixed to the bench at the required distance from the motor.

The shaker may be obtained from Messrs. Baird and Tatlock, Cross St., Hatton Garden, E.C.

Novel Synthesis of Tartaric Acid.—P. Genviesse.—By treating glyoxylic acid with nascent acid the author has obtained racemic acid. He thinks it not impossible that in nature tartaric acid is formed in an analogous manner.—*Comptes Rendus*, cxiv., No. 10.

* Exhibited at a meeting of the Chemical Society, March 6, 1892.

THE FARADAY CENTENARY.

The Faraday Centenary, in honour of Michael Faraday (born September 22, 1791), was celebrated at the Royal Institution of Great Britain on Wednesday, June 17, 1891, the Prince of Wales, K.G., F.R.S., in the chair.

The Prince of Wales opened the proceedings with the following Address:—

Ladies and Gentlemen,—I can well remember that two-and-twenty years ago I had the high privilege of presiding at a meeting here. That meeting was a very large one, and included many of the most eminent scientific men of the day. Among those present on that occasion, I remember, were the illustrious chemists, Prof. Dumas, Sir Edward Sabine, Sir Roderick Murchison, Sir Henry Holland,—a very old personal friend of mine,—Dr. Bence Jones, Mr. Warren de la Rue and many others, who I regret to say have now passed away. The object of our meeting on that occasion was to select a suitable memorial to the memory of the great Faraday, the eminent chemist and philosopher, who, I may say, was also the founder of modern electricity. As you are well aware, the fine statue by Foley, which is in the hall below, was, we thought, a suitable memorial to that great man. As for myself personally, I feel proud to think that in the days of my boyhood my brother and myself used to attend his chemical lectures here about Christmas time, and I shall ever remember the admirable and lucid way in which he delivered those lectures to us who were mere boys, and gave us a deep interest in chemistry which we kept up for many years, and which I had the opportunity of practising at the University of Oxford. I can only regret that I have not since had the time to pursue that interesting science. To-day is a memorable day, for this year we celebrate the centenary of the birth of that great man; and we all of us have reason to feel grateful that two such eminent men as Lord Rayleigh and Prof. Dewar should have consented to give lectures on the work of the great Faraday. I have only now to beg Lord Rayleigh to give us his address.

Lord Rayleigh said that the man whose name and work they were celebrating was identified in a remarkable degree with the history of this Institution. If they could not take credit for his birth, in other respects they could hardly claim too much. During a connection of fifty-four years, Faraday found there his opportunity, and for a large part of the time his home. The simple story of his life must be known to most who heard him. Fired by contact with the genius of Davy, he volunteered his services in the laboratory of the Institution. Davy, struck with the enthusiasm of the youth, gave him the desired opportunity, and, as had been said, secured in Faraday not the least of his discoveries. The early promise was, indeed, amply fulfilled, and for a long period of years by his discoveries in chemistry and electricity Faraday

maintained the renown of the Royal Institution and the honour of England in the eye of the civilised world. He should not attempt in the time at his disposal to trace in any detail the steps of that wonderful career. The task had already been performed by able hands. In their own *Proceedings* they had a vivid sketch from the pen of one whose absence that day was a matter of lively regret. Dr. Tyndall was a personal friend, had seen Faraday at work, had enjoyed opportunities of watching the action of his mind in face of a new idea. All that he could aim at was to recall in a fragmentary manner some of Faraday's great achievements, and, if possible, to estimate the position they held in contemporary science.

Whether they had regard to fundamental scientific import, or to practical results, the first place must undoubtedly be assigned to the great discovery of the induction of electrical currents. He proposed first to show the experiment in something like its original form, and then to pass on to some variations, with illustrations from the behaviour of a model, whose mechanical properties were analogous. He was afraid that these elementary experiments would tax the patience of many who heard him, but it was one of the difficulties of his task that Faraday's discoveries were so fundamental as to have become familiar to all serious students of physics.

The first experiment required them to establish in one coil of copper wire an electric current by completing the communication with a suitable battery; that was called the primary circuit, and Faraday's discovery was this:—That at the moment of the starting or stopping of the primary current in a neighbouring circuit, in the ordinary sense of the words completely detached, there was a tendency to induce a current. He had said that those two circuits were perfectly distinct, and they were distinct in the sense that there was no conducting communication between them, but, of course, the importance of the experiment resided in this—that it proved that in some sense the circuits were not distinct; that an electric current circulating in one does produce an effect in the other,—an effect which is propagated across a perfectly blank space occupied by air, and which might equally well have been occupied by vacuum. It might appear that that was a very simple and easy experiment, and of course it was so in a modern laboratory, but it was otherwise at the time when Faraday first made it. With all his skill, Faraday did not light upon the truth without delay and difficulty. One of Faraday's biographers thus wrote:—"In December 1824, he had attempted to obtain an electric current by means of a magnet, and on three occasions he had made elaborate and unsuccessful attempts to produce a current in one wire by means of a current in another wire, or by a magnet. He still persevered, and on August 29, 1831,—that is to say, nearly seven years after his first attempts,—he obtained the first evidence that an electric current induced another in a different circuit." On September 23rd, he writes to a friend, R. Phillips:—"I am busy just now again with electro-magnetism, and think I have got hold of a good thing, but cannot say; it may be a weed instead of a fish that, after all my labour, I at last haul up." We now know that it was a very big fish indeed. Lord Rayleigh proceeded to say that he now proposed to illustrate the mechanics of the question of the induced current by means of a model (see figure), the first idea of which was due to Maxwell. The one actually employed was a combination known as Huygen's gear, invented by him in connection with the winding of clocks. Two similar pulleys, A B, turn upon a piece of round steel fixed horizontally. Over these is hung an endless cord, and the two bights carry similar pendant pulleys, C D, from which again hang weights, E F. The weight of the cord being negligible, the system is devoid of potential energy; that is, it will balance, whatever may be the vertical distance between C and D. Since either pulley, A B, may turn independently of the other, the system is capable of two independent motions. If A B turn in the same direction and with the same velocity, one of the pendant pulleys, C D, rises, and the other falls. If, on the other hand, the motions of A B are equal and opposite, the axes of the pendant pulleys and the attached weights remain at rest. In the electrical analogue the rotatory velocity of A corresponds to a current in a primary circuit, that of B to a current in a secondary. If, when all is at rest, the rotation of A be suddenly started, by force applied at the handle or otherwise, the inertia of the masses E F opposes their sudden movement, and the consequence is that the pulley B turns *backwards*, *i.e.*, in the opposite direction to the rotation imposed upon A. This is the current induced in a secondary circuit when an electromotive force begins to act in the primary. In like manner, if A, having been for some time in uniform movement, suddenly stops, B enters into motion in the direction of the former movement of A. This is the secondary current on the break of the current in the primary circuit. It might perhaps be supposed by some that the model was a kind of trick. Nothing could be further from the truth. The analogy of the two things

was absolutely essential. So far was this the case that precisely the same argument and precisely the same mathematical equations proved that the model and the electric currents behaved in the way in which they had seen them behave in the experiment. That might be considered to be a considerable triumph of the modern dynamical method of including under the same head phenomena the details of which might be so different as in this case. If they had a current which alternately stopped and started, and so on, for any length of time, they, as it were, produced in a permanent manner some of the phenomena of electrical induction; and if it were done with sufficient rapidity it would be evident that something would be going on in the primary and in the secondary circuit. The particular apparatus by which he proposed to illustrate those effects of the alternating current was devised by a skilful American electrician, Prof. Elihu Thomson, and he had no doubt it would be new to many The alternating current was led into the electro-magnet by a suitable lead; if another electric circuit, to be called the secondary circuit, was held in the neighbourhood of that, currents would be induced and might be made manifest by suitable means. Such a secon dary circuit he held in his hand and it was

connected with a small electric glow-lamp. If a current of sufficient intensity were induced in that secondary circuit it would pass through the lamp, which would be rendered incandescent. [Illustrating.] It was perfectly clear that there was no conjuring there; the incandescent lamp brightened up. One of the first questions which presented itself was, what would be the effect of putting something between? Experimenting with a glass plate he showed there was no effect, but when they tried a copper plate the lamp went completely out, showing that the copper plate was an absolute screen to the effect, whatever it might be. Experiments of that kind, of course in a much less developed and striking form, were made by Faraday himself, and must be reckoned amongst some of his greatest discoveries.

Before going further, he might remark on what strong evidence they got in that way of the fact that the propagation of the electric energy which, having its source in the dynamo downstairs, eventually illuminated that little lamp, was not merely along the wires, but was capable of bridging over and passing across a space free from all conducting material, and which might be air, glass, or equally well, vacuum. Another kindred effect of a striking nature, devised by Prof. Elihu Thomson, consisted in the repulsive action which occurred between the primary current circulating around a magnet and the current induced in a single hoop of aluminium wire. Illustrating this by experiment, he showed that the repulsion was so strong as to throw the wire up a considerable height. Those effects were commonly described as dependent upon the mutual induction between two distinct circuits, one being that primarily excited by a battery or other source of electricity, while the other occurred in a detached circuit. Many surprising effects, however, depended on the reactions which took place at different parts of the same circuit. One of these he illustrated by the decomposition of water under the influence of self-induction.

About the time the experiments of which he had been speaking were made, Faraday evidently felt uneasiness as to the soundness of the views about electricity held by his contemporaries, and to some extent shared by himself, and he made elaborate experiments to remove all doubt from his mind. He re-proved the complete identity of the electricity of lightning and of the electricity of the voltaic cell. He evidently was in terror of being misled by words which might convey a meaning beyond what facts justified. Much use was made of the term "poles" of the galvanic battery. Faraday was afraid of the meaning which might be attached to the word "pole," and he introduced a term since generally substituted, "electrode," which meant nothing more than the way or path by which the electricity was led in. "Electric fluid" was a term which Faraday considered dangerous, as meaning more than they really knew about the nature of electricity, and as was remarked by Maxwell, Faraday succeeded in banishing the term "electric fluid" to the region of newspaper paragraphs.

Diamagnetism was a subject upon which Faraday worked, but it would take him too long to go into that subject, though he must say a word or two. Faraday found that whereas a ball of iron or nickel or cobalt when placed near a magnet or combination of magnets would be attracted to the place where the magnetic force was the greatest, the contrary occurred if for the iron was substituted a corresponding mass of bismuth or of many other substances. The experiments in diamagnetism were of a microscopic character, but he would like to illustrate one position of Faraday's, developed years afterwards by Sir Wm. Thomson, and illustrated by him in many beautiful experiments, only one of which he now proposed to bring before them. Supposing they had two magnetic poles, a north pole and a south pole, with an iron ball between them, free to move along a line perpendicular to that joining the poles, then, according to the rule he had stated, the iron ball would seek an intermediate position, the place at which the magnetic force was the greatest. Consequently, if the iron ball be given such a position, they would find it tended with considerable force to a central position of equilibrium; but if, instead of using opposite poles, they used two north poles, they would find that the iron ball did not tend to the central position, because that was not the place in which the magnetic force was the greatest. At that place there was no magnetic force, for the one pole completely neutralised the action of the other. The greatest force would be a little way out, and that, according to Faraday's observations, systematised and expressed in the form of mathematical law by Sir Wm. Thomson, was where the ball would go. (This was illustrated by experiment).

The next discovery of Faraday to which he proposed to call attention was one of immense significance from a scientific point of view, the consequences of which were not even yet fully understood or developed. He referred to the magnetisation of a ray of light, or what was called in more usual parlance the rotation of the plane of polarisation under the action of magnetic force. It would be hopeless to attempt to explain all the preliminaries of the experiment to those who had not given some attention to those subjects before, and he could only attempt it in general terms. It would be known to most of them that the vibrations which constituted light were executed in a direction perpendicular to that of the ray of light. By experiment he showed that the polarisation which was suitable to pass the first obstacle was not suitable to pass the second, but if by means of any mechanism they were able after the light had passed the first obstacle to turn round the vibration, they would then give it an opportunity of passing the second obstacle. That was what was involved in Faraday's discovery. (Experiment). As he had said, the full significance of the experiment was not yet realised. A large step towards realising it, however, was contained in the observation of Sir Wm. Thomson, that the rotation of the plane of polarisation proved that something in the nature of rotation must be going on within the medium when subjected to the magnetising force, but the precise nature of the rotation was a matter for further speculation, and perhaps might not be known for some time to come.

When first considering what to bring before them he thought, perhaps, he might include some of Faraday's acoustical experiments, which were of great interest, though they did not attract so much attention as his fundamental electrical discoveries. He would only allude to one point which, as far as he knew, had never been noticed, but which Faraday recorded in his acoustical papers. "If during a strong steady wind a smooth flat sandy shore with enough water on it, either from the receding tide or from the shingle above, to cover it thoroughly, but not to form waves, be observed in a place where the wind is not broken by pits or stones, stationary undulations will be seen over the whole of the wet surface. . . . These are not waves of the ordinary kind, they are (and this is the remarkable point) accurately parallel to the course of the wind." When he first read that statement many years ago he was a little doubtful as to whether to accept the apparent meaning of Faraday's words. He knew of no suggestion of an explanation of the possibility of waves of that kind being generated under the action of the wind, and it was, therefore, with some curiosity that two or three years ago at a French watering-place he went out at low tide on a suitable day when there was a good breeze blowing to see if he could observe anything of the waves described by Faraday. For some time he failed absolutely to observe the phenomenon, but after a while he was perfectly well able to recognise it. He mentioned that as an example of Faraday's extraordinary powers of observation, and even now he doubted whether anybody but himself and Faraday had ever seen that phenomenon.

Many matters of minor theoretic interest were dealt with by Faraday, and reprinted by him in his collected works. He was reminded of one the other day by a lamentable

accident which occurred owing to the breaking of a paraffin lamp. Faraday called attention to the fact, though he did not suppose he was the first to notice it, that by a preliminary preparation of the lungs by a number of deep inspirations and expirations, it was possible so to aërate the blood as to allow of holding the breath for a much longer period than without such a preparation would be possible. He remembered some years ago trying the experiment, and running up from the drawing-room to the nursery of a large house without drawing any breath. That was obviously of immense importance, as Faraday pointed out, in the case of danger from suffocation by fire, and he thought that possibly the accident to which he alluded might have been spared had the knowledge of the fact to which Faraday drew attention been more generally diffused.

The question has often been discussed as to what would have been the effect upon Faraday's career of discovery had he been subjected in early life to mathematical training. The first thing that occurred to him about that, after reading Faraday's works, was that one would not wish him to be anything different from what he was. I the question must be discussed, he supposed they would have to admit that he would have been saved much wasted labour, and would have been better *en rapport* with his scientific contemporaries if he had had elementary mathematical instruction. But mathematical training and mathematical capacity were two different things, and it did not at all follow that Faraday had not a mathematical mind. Indeed, some of the highest authorities had held (and there could be no higher authority on the subject than Maxwell) that his mind was essentially mathematical in its qualities, although they must admit it was not developed in a mathematical direction. With these words of Maxwell he would conclude:—"The way in which Faraday made use of his idea of lines of force in co-ordinating the phenomena of electric induction shows him to have been a mathematician of high order, and one from whom the mathematicians of the future may derive valuable and fertile methods."

Sir William Thomson, in moving a vote of thanks to Lord Rayleigh for his lecture, said that the Royal Institution was during the last part of Faraday's life, and during the whole of his scientific career, his home. The splendid results of Faraday's labours contributed in no small degree to the scientific glory of the Nineteenth Century, and helped to make it one of the most prolific periods in the world's history. Faraday was throughout animated solely by the love of knowledge. He freely gave his discoveries to mankind, and left it to others to turn them to practical and profitable account.

Sir George Stokes, in seconding the motion, said that he had had the honour of a personal acquaintance with Faraday, whose single-minded devotion to knowledge for its own sake was beyond all praise.

The vote of thanks was cordially passed.

Lord Rayleigh, in acknowledgment, said that it had been a great honour and a great responsibility which had been placed upon him. He remembered with gratitude the instruction which he had derived at Cambridge from Sir Gabriel Stokes, and felt deeply indebted to Sir William Thomson for all that he had learned from his writings and his conversation.

Sir Frederick Bramwell read the following letter from Dr. Tyndall:—

Hind Head House, Haslemere,
June 16, 1891.

Dear Sir Frederick Bramwell,

As Faraday recedes from me in time, he becomes to me more and more beautiful. Anything, therefore, calculated to do honour to his memory must command my entire sympathy.

But the utmost liberty I can now allow myself is to be shifted from my bed to a couch and wheeled to a position near the window, from which I can see the bloom of the gorse and the brown of the heather.

Thus, considerations affecting the body only present an insuperable barrier to my going to London on Wednesday.

Yours very truly,
John Tyndall.

The Duke of Northumberland then asked the meeting to express its sense of the kindness of his Royal Highness in presiding, and said he had permission to read two letters written many years ago, proving how keen was the interest taken by him in the lessons he had received from Faraday. The letters were as follows, the first being addressed to Mr. Faraday, and the second to Mrs. Faraday on the occasion of her husband's death:—

Windsor Castle, January 16, 1856.

Dear Sir,

I am anxious to thank you for the advantage I have derived from attending your most interesting lectures. Their subject I now feel is of great importance. I hope to follow the advice you gave us of pursuing it beyond the lecture room, and I can assure you that I shall always cherish with great pleasure the recollection of having been assisted in my early studies in chemistry by so distinguished a man.

Believe me, dear sir, yours truly,
Albert Edward.

Wiesbaden, September 10, 1867.

Dear Mrs. Faraday,

Although I have not the pleasure of knowing you, I cannot resist sending you a few lines to tell you how deeply grieved and distressed I am to hear of the death of your husband, Professor Faraday. Having had the great pleasure of knowing him for some years, and having heard his interesting lectures already when quite a boy, I can fully appreciate how great the loss must be, not only to you, but to the whole country at large, where his name was deeply venerated by all classes. His name will not only be remembered as a great and distinguished scientific man, but also as a good man, whose excellent and amiable qualities were so universally known. Pardon me trespassing so soon on your great grief, and

Believe me, dear Mrs. Faraday, yours very sincerely,
Albert Edward.

The Duke of Northumberland continued: He thought they would all agree that that was a touching letter of condolence. His Royal Highness had now long been a patron of the Institution, and had watched its progress with interest, which he hoped would be continued. He trusted his Royal Highness would have the gratification of seeing the country prosper long under the rule of his august family, and of seeing the benefits of science resulting in the increased happiness of the people.

Sir W. Grove seconded the resolution, and said he was possibly the only one in the room who had known Faraday in his prime. He wished they had been celebrating the centenary with Faraday alive.

The thanks of the meeting to His Royal Highness having been expressed by acclamation,

The Prince of Wales acknowledged it as follows:—Ladies and Gentlemen, I feel that I cannot, out of courtesy to yourselves, and of the noble duke who has so kindly proposed the usual thanks, and to Sir William Grove who has given us an interesting speech, pass it by without expressing to you my warmest thanks. It is a great honour and privilege to me to preside on this most interesting and memorable occasion. I have now known this room for thirty-six years, and I agree with Sir William Grove in wishing that we were celebrating the centenary of Faraday alive, and not dead—that he was alive to spend his hundredth birthday among us. I feel every time I come into this room as if I can see him standing there at that table, where he gave his interesting lectures and experiments when I was a boy. I again tender my thanks

to you, as I do to Lord Rayleigh, for the most interesting lecture he has given.

There was an exhibition in the Library of memorials of Faraday kindly lent to the Institution by Miss Jane Barnard and others.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 3rd, 1892.

Prof. A. Crum Brown, F.R.S., President, in the Chair.

Concluded from p. 140).

*116. "*Contributions to our Knowledge of the Aconite Alkaloids.* Part III. *The Formation and Properties of Aconine and its Conversion into Aconitine.* By Professor W. R. Dunstan and Dr. F. W. Passmore.

Owing to the uncertainty which exists with reference to the product of the hydrolysis of aconitine, the authors have re-investigated the subject, using a pure alkaloid. Wright and Luff have stated that when aconitine is hydrolysed the sole products are aconine and benzoic acid. More recently, however, Dragendorff and Jürgens have asserted that the hydrolysis occurs in two stages, their contention being that benzoic acid and an alkaloid identical with the picraconitine isolated by Wright and Luff from the roots of supposed *Aconitum napellus* are formed in the first stage, while in the second stage the picraconitine is hydrolysed into benzoic acid, methyl alcohol, and aconine, which last is the final product of hydrolysis.

The authors have carefully hydrolysed pure aconitine by heating it with water in closed tubes at 150°, but have been unable to obtain at any stage either picraconitine or methyl alcohol. The alkaloid extracted from the solution by ether was proved to be a mixture of aconine with unaltered aconitine. Using pure aconitine, action occurs precisely in accordance with the equation—

$$C_{33}H_{45}NO_{12}+H_2O=C_{26}H_{41}NO_{11}+C_7H_6O_2,$$

leaving little doubt that aconitine is benzoyl-aconine.

Although attempts to establish the correctness of this inference by heating aconine with benzoic anhydride were without result, anhydroaconitine was eventually obtained by the interaction of aconine and ethylic benzoate at 130°: as the anhydro-compound is convertible into aconitine, the partial synthesis of the alkaloid thus effected leaves no doubt that it is benzoylaconine.

Up to the present time, neither aconine nor its salts have been obtained in a crystalline state. The authors have hitherto been unsuccessful in all their attempts to crystallise aconine, but they have succeeded in crystallising several of its salts, viz., the chlorhydride, bromhydride, sulphate, and nitrate. All these salts are very soluble in water, the chlorhydride being least soluble and the easiest to crystallise: it is best prepared by crystallisation from a mixture of alcohol and ether; when dried at 100° it melts at 175·5° (corr.). The crystals deposited from alcohol have the composition—

$$C_{26}H_{11}NO_{11},HCl,2H_2O.$$

When dried at 100° they still retain one molecular proportion of water, which is, however, lost at 120°. The aqueous solution is lævorotatory: $[\alpha]_D = -7·71°$. It combines with auric chloride, forming an aurichloride considerably more soluble than the corresponding aconitine salt.

Aconine was prepared from the pure chlorhydride by adding silver sulphate and subsequent treatment of the aconine sulphate with exactly sufficient baryta water. The solution on evaporation furnished a hygroscopic brittle gum which refused to crystallise; this melted at 132° (corr.), and on analysis it afforded numbers agreeing with the formula $C_{26}H_{41}NO_{11}$, which is that proposed by Dunstan and Ince from the results of their study of pure aconitine. Aconine is very soluble in water; the aqueous solution is alkaline. When dry it is insoluble in ether and almost insoluble in chloroform. It is a powerful reducing agent, precipitating the metals from solutions of gold and silver salts; it also reduces Fehling's solution. The physiological action of pure aconine is being investigated. Its aqueous solution is slightly bitter and gives rise to a burning sensation in the mouth, but does not produce the tingling which is characteristic of aconitine. In respect of its action on polarised light aconine exhibits the same peculiarity as aconitine. Its salts are lævorotatory, whilst a solution of the alkaloid is dextrorotatory, $[\alpha]_D + 23°$. When heated with alkalis aconine slowly resinifies.

The examination of various agents on aconine has so far not led to any important results. Nitrous acid fails to attack it. The principal product of its oxidation by alkaline permanganate is oxalic acid. Attempts to isolate an additive compound with methyl iodide have been unsuccessful.

By the action of methyl iodide on aconitine a crystalline *aconitine methiodide* ($C_{33}H_{45}NO_{12}\cdot CH_3I$) was obtained, which melts at 219° (corr.). The *aconitine methydroxide* prepared from the compound—

$$(C_{33}H_{45}NO_{12}\cdot CH_3OH)$$

is amorphous, and the salts which it yields do not appear to crystallise. A further study will be made of this compound, and its physiological action will be investigated.

At the conclusion of the paper Professor Dunstan exhibited and described a simple laboratory shaking appliance devised by Mr. Dymond and himself, an account of which is to be found at p. 148.

Discussion.

Mr. Howard said that the important conclusion now arrived at by the authors as to the nature of the alkaloids of pure *Aconitum napellus* illustrated the value of the botanist and chemist working together; it was to be expected that their co-operation would lead to other valuable results in the future, as the success achieved in increasing the yield of cinchona alkaloids would probably lead to progress being made in increasing the medicinal value of other plants.

Professor Thorpe questioned the desirability of associating an old name with a new alkaloid.

The President expressed a similar opinion, citing the case of thiosulphate and hyposulphite in illustration of the confusion sometimes caused by such action.

Professor Dunstan, in his reply, said that the investigation had been made possible in the first instance only through the liberality of Mr. Howard, who gave them no less a quantity than an ounce of aconitine extracted by a known process from *A. napellus*. Napelline was a name which had been very little used, and it was very difficult to devise a better appellation for the new alkaloid.

*117. "*Note on the Carbon Deposited from Coal-gas Flames.*" By Wm. Foster, M.A.

The author quotes analyses of cokes obtained by carbonising sugar and starch:—

	Carbon.	Hydrogen.
Cane-sugar coke—high temperature	95·0	1·1
" " low "	94·1	1·2
Starch coke..	95·0	0·9

From the similarity in composition of these cokes to that of the soot obtainable from coal-gas flames, he is of opinion that there is a resemblance in the general character of the chemical processes whereby they are formed.

*118. "*The Volumetric Estimation of Mercury.*" By Chapman Jones.

The author has found the cyanide method of estimating

mercury suggested by Hannay (*C. S. Journ.*, 1873, 565) and modified by Tuson and Neison (*ibid.*, 1877, xxxii., 679) to be unsatisfactory, the presence of carbon dioxide interfering with the titration. If, however, instead of adding the potassium cyanide solution until the turbidity produced by ammonia disappears, the titration be finished by adding, with certain precautions, a standard mercury solution until a definite and permanent turbidity is produced, concordant results are readily obtained. The method of working described is, if necessary, to separate the mercury as sulphide, and dissolve the washed precipitate in cold *aqua regia*, and to dilute and filter the solution. For the titration litmus extract is added and neutralisation effected with solid potassium carbonate and hydrogen chloride, and finally with dilute ammonia. Excess of the cyanide solution is added, then a slight excess of ammonia, and, lastly, a standard solution of mercuric chloride, until a permanent turbidity is obtained equal to that produced by 0·1 c.c. of the mercury solution in water containing about the same amounts of litmus and ammonia as the solution which is being titrated.

119. "*Chromic Acid.*" By ELEANOR FIELD, Bathurst Student of Newnham College, Cambridge.

According to Moissan (*Ann. Chim. Phys.* [6], v., 568) it is possible to obtain crystals of the compound H_2CrO_4 by cooling with ice a solution saturated with CrO_3 at 90°. In the present notice results are quoted which show that the crystals obtained on following Moissan's directions are but those of CrO_3.

The molecular weight of the dissolved substance calculated from the effect of CrO_3 on the boiling-point of water was found to be only 57, which is far below the theoretical value, viz., $CrO_3 = 100·4$. Ostwald, from determinations of the lowering of the freezing-point of water produced by CrO_3, came to the conclusion that the aqueous solution contains $H_2Cr_2O_7$ dissociated into three ions: by trebling the mean value deduced from the boiling-point experiments, the value 171·85 is obtained, a number which does not agree either with the molecular weight of H_2CrO_4 (118·4) or with that of $H_2Cr_2O_7$ (218·8).

120. "*The Origin of Acetylene in Flames.*" By Prof. V. B. LEWES.

The author has sought to determine whether acetylene is the product of high temperature change or of oxidation. The experiments described consisted in passing hydrocarbon gases and mixtures of such gases with others through a heated platinum tube 2 m.m. in diameter, which, judging from experiments made to test the point, would seem to be without special action.

On passing methane alone through the tube while a length of 6 inches was heated to 1100° in the flat flame of a broad Bunsen, a product was obtained containing 3·2 per cent of unsaturated hydrocarbons and 1·8 per cent of acetylene. The effect of heating methane with other gases is indicated by the following figures:—

	3 per cent oxygen.	15 per cent air.	50 p.c. carbon monoxide.	60 per cent hydrogen.
Unsaturated hydrocarbons	2·0	2·0	1·0	1·47
Acetylene	1·426	0·656	0·887	0·473
Carbon monoxide	1·1	1·0	—	0·490

These results appear to point to acetylene being formed by the action of heat alone.

Ethane heated alone gave a product containing 19·47 per cent unsaturated hydrocarbons and 3·224 per cent of acetylene. The effect of heating ethane diluted with 30 per cent of hydrogen with air was as follows:—

	15 p.c. air.	20 p.c. air.	25 p.c. air.
Unsaturated hydrocarbons	7·69	5·58	5·05
Acetylene..	3·39	3·20	3·11
Carbon dioxide..	0·00	1·01	1·51
„ monoxide	1·54	2·53	3·03

The effect of temperature on the formation of acetylene is well shown by the following results obtained on converting Russian petroleum into oil-gas in a Patterson retort:—

Temperature of retort ..	500°	700°	800°	900°
Yield of gas per gallon of oil	12 c.p.	60 c.p.	72 c.p.	84 c.p.
Illuminating power	54·8	50·7	57·1	42
Unsaturated hydrocarbons	39·13	36·56	36·55	22·04
Acetylene	0·052	0·084	0·38	0·46

Anniversary Meeting and Second Anniversary Dinner.

A letter in the following terms has been issued by the Secretaries to all Fellows on the Home list:—

"We have the honour to inform you that the Society's Second Anniversary Dinner is to take place at the Hôtel Métropole on Wednesday, March 30th, at seven for half-past seven o'clock, the Anniversary Meeting being appointed to take place at Burlington House at 4 o'clock in the afternoon of the same day.

"The price of the dinner, including wine, will be One Guinea, payable in advance.

"We beg to request that you will return the enclosed post-card duly filled in not later than March the 19th.

"A ticket admitting to the dinner will be sent to you on receipt of £1 1s., the price of the dinner ticket."

PHYSICAL SOCIETY.

March 11th, 1892.

Professor A. W. RÜCKER, F.R.S., Vice-President, in the Chair.

MR. H. M. ELDER, M.A., read a paper on "*A Thermodynamical View of the Action of Light on Silver Chloride.*"

In the decomposition of silver chloride by light chlorine is given off, and a coloured solid body of unknown composition (sometimes called "photochloride") formed, the reaction being indicated by the formula—

$$nAgCl = Ag_nCl_{n-1} + \tfrac{1}{2}Cl_2.$$

If the experiment be carried out in a sealed vacuum the chloride is darkened up to a certain point, but regains whiteness when left in the dark. These facts have led the author to believe that the pressure of the liberated chlorine is a function of the illumination or intensity of light falling upon the chloride, in the same way as the pressure of a saturated vapour is a function of the temperature. Since illumination is a quantity in many respects analogous to temperature, he considers it not unreasonable to apply thermodynamic arguments, and regard chlorine, in presence of silver chloride and "photochloride," as the working substance in a "light engine." He therefore supposes a Carnot's cycle to be performed on the substances at constant temperature, the variables being pressure, volume, and illumination.

Since the cycle is strictly analogous to Carnot's, except that illumination is written for temperature, he infers that the efficiency is a function of the two illuminations. It also follows that just as Carnot's cycle is used to determine an absolute scale of temperature, so this cycle may be applied to determine an absolute scale of illumination. It only remains to determine an empiric scale analogous to the air thermometer, and to compare it with the photodynamic scale provided a method of making the comparison can be devised.

Assuming the axioms applied to Carnot's cycle are true when illumination is written for temperature, the author shows mathematically that $p \propto I^{\rho/T}$, where p is the pressure, I the illumination, T the absolute temperature, and ρ the heat of combination per grm.-molecule of chlorine evolved. If P be the heat of formation of silver chloride the fraction ρ/P may be considered as expressing the fraction of the total chlorine that can be removed by the action of light upon it, supposing the gas removed so as

to keep the pressure below that corresponding to the illumination. The chemical equation might then be written $P/\rho AgCl = Ag_{P/\rho}Cl_{P/\rho-1} + \frac{1}{2}Cl_2$; thus the formula for "photochloride" would be $Ag_{P/\rho}Cl_{P/\rho-1}$.

Prof. Rücker read a letter from the President (Prof. Fitzgerald) on the subject of the paper. He inquired what axiom corresponding with the second law of thermodynamics was employed. He was not sure that the engine was perfectly reversible, and felt doubt on the subject of phosphorescence mentioned in the last operation of the cycle. Nevertheless the paper was a most interesting one and very suggestive.

Prof. Herschel pointed out that Becquerel's phosphoroscope showed that all kind of light produced phosphorescence, and thought that in considering the subject, the non-thermal character of photogenic light should be kept in view.

Mr. Baker said he had been working on silver chloride for several years, and found that no darkening whatever took place if kept dry *in vacuo*. He considered oxygen necessary to the action.

Dr. C. V. Burton, referring to the motivity of the system, said that only a small fraction of the energy of the illumination was actually made use of. He also thought it necessary to consider how far the second law of thermodynamics could be treated as an axiom. He himself had been led to believe the law did not hold for mixtures of substances differing in a finite degree from one another. Some time ago he experimented on a solution of sodium sulphate placed in a dialyser and kept at constant temperature. The more acid portion passed through the membrane, and on mixing, a rise of temperature was observed; the dialyser thus acted like Maxwell's demons, and the mixing increased the motivity of the system.

Prof. Rücker expressed his doubts as to whether the cycle described in the paper was strictly analogous to that in Carnot's problem. In the latter case the parts of the working substance only differed infinitesimally from one another, whilst in the former the working body was a mixture of two solids and a gas. In order that the increased illumination should not alter the temperature, heat must be carried away. According to the paper the first part of the cycle must be both adiabatic and isothermal. This seemed hardly possible. If the chlorine alone be considered it could not be true, and it could only hold if the chloride absorbed all the heat given out by the compression of the chlorine. This seemed improbable, but if true it would be very important.

Capt. Abney saw another difficulty in the fact that at low temperatures silver chloride is not acted on, even by violet light, whereas heating greatly increases the action. In his opinion the conclusions arrived at required confirmation, but the paper would form a starting point for many new experiments.

Mr. Elder, in reply to Prof. Fitzgerald, said the axiom corresponding to the second law, as stated by Clausius, might be formulated thus: Energy cannot of itself pass from a less bright to a brighter body. In the paper he had assumed that the energy given out during compression at the lower illumination was of the same quality as that absorbed at the higher. The whole question depended on comparisons of intensities of illuminations of different wave-lengths. In the expression $p \propto I^{\rho/T}$, ρ was probably a function of T, and Capt. Abney's objection was not necessarily fatal.

Speaking of the presence of oxygen being essential to decomposition, he believed some sensitising body was necessary, but judging from experiments he had seen an infinitesimal quantity would probably be sufficient, for the action seemed to be of a catalytic nature. He felt the weight of Prof. Rücker's objections, but thought they might possibly be met.

A paper on "*Choking Coils*" was read by Prof. Perry, F.R.S. Regarding a choking coil as a transformer with one primary and many secondaries, represented by the conducting masses, he pointed out that all the secondaries might be replaced by a single coil of n turns, and resistance r ohms, short-circuited on itself. Assuming no magnetic leakage the equations for the two circuits at any instant are $V = RC + N\theta I$ and $o = rc + n\theta I$, where N and n are the turns, R and r the resistances, I the total induction in 10^8 C.G.S. lines, and C and c the primary and secondary currents respectively.

Since the exciting current C is all important in choking coils and its value depending on the law of magnetisation, the equations are treated in a different manner to that adopted in ordinary transformer calculations. Expressing the magnetic law as a Fourier series, $I = \Sigma A_i \rho_i \sin ix$, the value of A (viz., $NC + nc$) is deduced, and when V or I is given as a periodic function of the time, C may be calculated.

Assuming $V = V_0 \sin kt$, the author finds—

$$C = \frac{V_0}{N^2 \sigma k}\left[\sqrt{1 + 2e\sin f + e^2}\,.\,\sin\left\{kt - 90 + \tan^{-1}\left(\tan f + \frac{e}{\cos f}\right)\right\} - b\cos 3kt - m\cos 5kt\right]$$

where $e = n^2 \rho k/r$, f is the hysteresis term, and b and m constants depending on the law of magnetisation. For ordinary transformer magnetisation $b = 0{\cdot}2$ and $m = 0{\cdot}05$.

From the above expression it will be seen that if there is no hysteresis (*i.e.*, $f = 0$) the effect of the eddy currents, e, is to increase the amplitude of the important term and to produce a lead of $90° - \cot^{-1} e$, whereas the effect of hysteresis without eddy currents is to leave the amplitude unaltered and produce a lead f. Putting $f = 0$ gives results in accordance with experimental observation; hence the author is inclined to believe that there is no hysteresis in transformers. He also points out that the higher harmonics must exist, and thinks it probable that a choking coil with finely divided iron may prove a method of increasing frequency by mere magnetic means.

Taking the case of a 1500 watt transformer (2000 volts) unloaded, in which the loss in eddies was 40 watts, it is shown that a secondary of 2 turns and resistance 1·9 ohms would replace the eddy current circuits. Assuming constant permeability and no eddy currents, the value of C comes out $0{\cdot}07398 \sin (kt - 90°)$, whilst with eddy currents and some saturation $C = 0{\cdot}07911 \sin (kt - 69{\cdot}2°) - 0{\cdot}014796 \cos 3kt - 0{\cdot}003695 \cos 5kt$.

Dr. Fleming said he was working on the subject of choking coils, and had found that in closed circuit transformers unloaded the real watts were about 0·7 times the apparent watts. This, on the assumption of sine functions, would indicate a lag of about 45°. A similar rule for open circuit transformers was much needed. It was important to know what size of core and coil was required to choke down to a given current.

Dr. Sumpner thought it better to treat the subjects graphically rather than by analysis, and described a construction whereby the fundamental equations could be readily integrated.

Prof. Perry said he had reason to think that ordinary hysteric curves were not applicable to transformers. By analysis of the experimental E.M.F. and current curves, one could work backwards and find the true hysteresis curves.

Synthesis of the Minerals Crocoite and Phornicochroite.—C. Ludeking.—These syntheses may be affected by exposing a solution of lead chromate in potassa to the air for some months in a flat-bottomed vessel. Sometimes a mixture of the two kinds of crystals is obtained. The composition of the crystals is the same as that of the natural minerals. Phornicochroite is obtained alone if the chromate is employed on employing the chromate with a large excess of concentrated potassa. If we use an excess of lead chromate along with potassium chromate crocoite is produced alone.—*Comptes Rendus.*

NOTICES OF BOOKS.

The Ilford Manual of Photography. By C. H. Bothamley, F.I.C., F.C.S.S. (London and Berlin). Small 8vo., pp. 207. London: The Britannia Works Co., Ltd., Ilford.

The standpoint of this manual is very clearly defined in the preface. It has been compiled for the benefit of the large number of photographers "who apply the art to pictorial, technical, or scientific purposes." Now, the wants of those who wish to photograph landscapes or to take portraits are very fully and ably met; but such as wish to apply photography to astronomical, meteorological, geological, or biological purposes, will here find little guidance. This we must regret to see, especially as the author is a master of the art of exposition. Those who are chiefly interested in the "experimental side of photography" are recommended to look elsewhere.

On the subject of shutters Mr. Bothamley is not very diffuse. For general purposes he recommends the Thornton-Pickard shutter, which he describes and figures. For very rapid exposure he admits that some special form of shutter is to be used, though he does not guide the tyro or the amateur in the difficult task of selection. "Difficult," we say, as a number of makers are each declaring that their especial devices are the best.

We are glad to see that the author cautions intrusive photographers—and we must confess that such persons exist—against surreptitiously introducing their "kodaks" or other detective hand-cameras into private premises. The most offensive of such Paul Pry's are those who try in this manner to take photographs of plant or machinery.

The chapter on photography by artificial light will be very useful in a climate like ours, where fog and cloud interfere so largely with natural light. The reader is warned that magnesium flash powders are in reality explosives, and must be dealt with as such. The precautions laid down by the author, if duly followed, will suffice to guard against any disastrous results.

Orthochromatic plates are recognised as highly useful, or rather indispensable, for photographing objects under the microscope. This information is about all which we have been able to find specially addressed to the microphotographer.

For the practical photographer who turns his attention to scenery or portraiture,—in other words to fully 90 per cent of the fraternity—this manual is highly to be recommended.

The Optical Lantern as an Aid in Teaching. By C. H. Bothamley, F.I.C., F.C.S. London: Hazell, Watson, and Viney, Ltd.

The magic lantern, as it was called of yore, has in these days not merely undergone great improvements, but is being put to more dignified uses. The lantern as an auxiliary in school and college teaching is in many cases superseding the microscope, which can only be examined by one disciple at a time, and, except for geometrical diagrams, it must certainly consign the blackboard and chalk to oblivion.

Mr. Bothamley opens his subject with certain dry remarks on the system of instruction pursued until lately in ordinary schools. Of this kind of instruction he gives some striking examples. "Some of us have heard, too, of examinees in biology who had never looked through a microscope, and of so-called teachers of chemistry whose only apparatus was a blackboard and a piece of chalk." He does not add, as he might, that the "examinee in biology" *passed*, to the disgrace of the examiner, and of the entire educational system. Nor does Mr. Bothamley hint at the reason why mere verbalism, mere memory-work, has been so exclusively exalted.

An examiner can easily tell to what extent the memory of a student has been cultivated, and how far it has been systematically directed to certain specified subjects. But to ascertain how far the youth has acquired the arts of acute and accurate observation, and of drawing right conclusions from the phenomena recognised, he is necessarily impotent. Hence, in countries where examinationism is rampant, education is made to consist more or less exclusively of mere memory-work; the physical and natural sciences are thrust into the background.

The old belief that the lantern can be successfully used only in a darkened room has been overturned by Mr. L. C. Miall, Professor of Biology at the Yorkshire College, Leeds. This is a great step in advance. We remember long years ago giving a lecture on the properties of phosphorus and its compounds before a promiscuous audience. The room was darkened whilst bubbles of hydrogen phosphide were allowed to ascend into a large glass receiver of oxygen gas. One of the lightning-like flashes revealed to the audience a boy in the act of very devoutly kissing a girl who was sitting close to him. We need scarcely say that this experiment very much interfered with the attention of the younger portion of the spectators.

Good instructions are here given for the position of the lecture-table, the lantern, and the screen. It is remarked that "at the Yorkshire College the number of slides required by the various departments is so large that the whole time of a special photographic assistant is occupied with their production."

Good practical instructions are here given on the manipulation of the lantern. The teachings of this little book are a not unimportant step in the much needed direction of school-reform.

CORRESPONDENCE.

LABORATORY STILLS.

To the Editor of the Chemical News.

Sir,—Will any of your readers kindly tell me the state of the law in relation to stills? I have a small still in use in my laboratory for distilling water, and am now informed by the Inland Revenue Office that I must pay a license for same, and am liable to an immense number of penalties for using same without express permission. As I never heard or dreamt that any license was required to distil *water*, I shall be glad to have further information on this subject. It seems that the law tries all it can to crush scientific progress in this country.—I am, &c.,

W. J. Cooper.

Detection of Saccharin.—D. Vital (*L'Orosi*).—The author proposes three methods. For this purpose the substance in question is mixed with three or four times its volume of slaked lime, and heated slowly to redness in a glass tube. There are obtained ammonia, calcium carbonate and sulphate, and phenol, which condenses in small drops in the cooler parts of the tube. The three former products are recognised by the usual methods. For the detection of phenol the author proposes the following reaction:—A few crystals of potassium chlorate are cautiously placed in a few c.c. of concentrated sulphuric acid; a drop of this solution is put in a porcelain capsule, and a glass rod moistened with the above-mentioned condensed product is plunged into it. There appears a green colouration which changes to an intense blue. The second method consists in treating the isolated saccharin with concentrated sulphuric acid. Benzoic acid is formed. The third method agrees with that of Schmitt and Pinette, who heat with caustic soda. The products are ammonia, salicylic acid, and sulphuric acid.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 10, March 7, 1892.

Fermentation of Blood.—MM. Berthelot and G. André.—The authors have operated upon a specimen of ox-blood, collected at the abattoir, and freed from fibrine. Its specific gravity at 15° was 1·045. Its fermentation lasted 130 days in a water-bath heated to 35°, and raised at the conclusion to 45°. The products are carbonic acid and ammonia, volatile fatty acids, and fixed nitrogenous principles. The carbonic acid was free from hydrogen and nitrogen, but contained traces of hydrogen sulphide and of ammonia. The proportion of ammonia formed is very considerable, two-thirds of the nitrogen of the albuminoid matters having been changed into ammonia by fermentation. The other third part of the nitrogen remains after fermentation in a fixed state. The fatty acids belonged exclusively to the series $C_nH_{2n}O_2$. The whole of the series was present from the formic to the caproic, and beyond. The fixed nitrogenous principles were resolved into four groups:—(1) an insoluble compound of a humic nature; (2) polynitrogenous acid forming soluble, crystalline barium salts; (3) a neutral or acid compound, soluble in absolute alcohol and non-crystalline; (4) alkaline salts, insoluble in alcohol.

Densities of Aqueous Solutions.—G. Charpy.—The contraction observed only in aqueous solutions corresponds either to a peculiarity in the constitution of the mol. of water, or to the existence in the midst of the solution or true chemical compound.

The Combinations of Gaseous Ammonia with Boron Bromide and Iodide.—A. Besson.—The bromine compound is a white amorphous body of the composition $BBr_3,4NH_3$. It is decomposed by water and by alkalis. The iodide is also a white amorphous solid, $BI_3,5NH_3$. It turns yellow on exposure to light, with the liberation of a small quantity of iodine. It is decomposed if heated in a current of hydrogen and is also decomposed by water.

Value of the Primary Alcohol Function.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

Transformation of Cupreine into Quinine Di-iodomethylate.—E. Grimaux and A. Arnaud.—The authors, in reply to a memoir by Dr. Hesse in the *Annalen der Chemie*, October 15, 1891, maintain that the transformation is almost total.

Rapidity of the Decomposition of the Diazo-Compounds by Water.—P. Th. Müller and J. Hausser.—This decomposition is very slow at ordinary temperatures, but increases in rapidity with the rise of temperature. The rate of decomposition can be estimated by measuring the volumes of gas liberated.

Action of Capryl Iodide upon Trimethylamine in an Aqueous Solution in Equimolecular Proportion. Formation of Dimethylcaprylamine in Heat and of Caprylene in Cold.—H. and A. Malbot.—In heat we obtain four products: dimethylcaprylamine, tetramethylammonium iodide, trimethylamine hydriodate, and caprylene. In the cold we obtain merely the two latter products. In heat the most important product is dimethylcaprylamine, but in cold it is caprylene.

On Two Novel Species of Streptothrix and on the Place of this Genus in Classification.—C. Sauvageau and M. Radaes.—Cohn's *Cladothrix* is certainly a bacterium decidedly distinct from Cohn's *Streptothrix* and Harz's *Actinomyces*. The latter are *hyphomyces*, which must both disappear as genera and be returned to Wallroth's genus *Oospora*.

MEETINGS FOR THE WEEK.

Monday, 28th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Mine Surveying," by Bennett H. Brough, Assoc.R.S.M.
Tuesday, 29th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Society of Arts, 8. "The Decorative Uses of Sculpture," by E. Roscoe Mullins.
Wednesday, 30th.—Society of Arts, 8. "Foreign Exchange," by Ewing Matheson.
—— Chemical, 4. (Anniversary). President's Address. Election of Office Bearers and Council.
Thursday, 31st.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Epidemic Waves," by B. Arthur Whitelegge, M.D., B.Sc.
Friday, April 1st.—Royal Institution, 9. "The Motion of the Ether near the Earth," by Prof. Oliver Lodge, F.R.S.
—— Geologists' Association, 8.
—— Quekett Club, 8.
Saturday, 2nd.—Royal Institution, 3. "Dramatic Music, from Shakspeare to Dryden," by Prof. J. F. Bridge, Mus. Doc.

Errata.—P. 144, col. 1, the composition of hæmocyanine should read as follows:—$C_{887}H_{1398}N_{232}CuS_4O_{246}$. In the paper on "Ptomaines" the formula for the alkaloid extracted from urine in cases of whooping-cough should be $C_5H_{10}NO_3$. And the sentence commencing "Afanassieff's, &c.," should read—"Afanassieff's bacillus gives rise to the same alkaloid as that extracted from urine in cases of whooping-cough."

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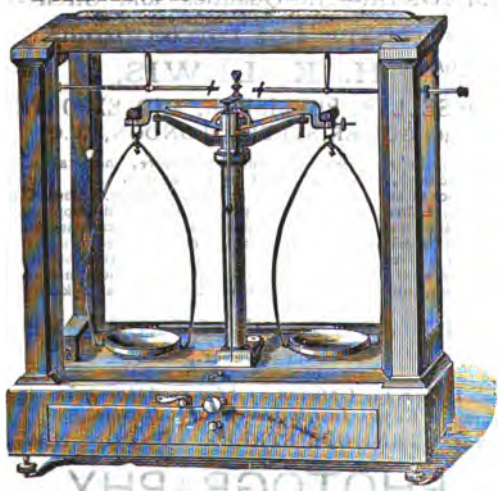

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THE CHEMICAL NEWS.

Vol. LXV., No. 1688.

A "CHEMISTS' BENEVOLENT FUND."*

Resolution of Council, passed November 19, 1891:—

"That a Committee be appointed to consider the letters from Prof. Attfield, of October 2 and November 16, 1891, relating to a Chemists' Benevolent Fund, and to report as to the course of action they deem most prudent for the Council to take with regard to the matter.

"That the Committee consist of:—Sir F. A. Abel, F.R.S., Prof. A. Crum-Brown, F.R.S., Dr. J. H. Gladstone, F.R.S., Dr. Hugo Müller, F.R.S., Prof. W. Odling, F.R.S., Dr. W. J. Russell, F.R.S., Prof. T. E. Thorpe, F.R.S., Prof. J. M. Thomson."

Report.

1. Your Committee beg to report that they have held four meetings on the subject, and have given careful consideration to the proposal for the foundation and administration by, or in connection with, the Chemical Society of a "Chemists' Benevolent Fund," as set forth in Prof. Attfield's letter of November 16, addressed to members of the Council, and more fully in his circular of October 2, 1891. Your Committee at one of their meetings had the advantage of Prof. Attfield's attendance, and have since been in further communication with him.

2. Your Committee, while sympathising with the general object sought to be attained, and making hearty acknowledgment of the zeal displayed by Prof. Attfield in the steps taken by him to initiate the proposed Fund, feel that they have been placed in a position of some difficulty by reason of the indefinite character of the particular proposal presented for their consideration.

3. In his letter of November 16, Prof. Attfield refers members of the Council to his circular of October 2, as "containing the conditions under which the contributions were obtained;" but neither from this circular nor from Prof. Attfield himself, by whom alone these conditions appear to have been propounded, have your Committee been able to ascertain which of the somewhat vaguely expressed conditions set forth in the circular are to be regarded as mere suggestions for the consideration of, and which as stipulations obligatory upon, the administrators of the proposed fund, in order to entitle them to the contributions so generously promised thereto.

4. So far as your Committee can gather, however, it was Prof. Attfield's intention to invite contributions to a Fund to be founded in celebration of the Jubilee of the Chemical Society, and to be dealt with as follows:—(1) "The *supervision*, at least, of both foundation and administration," to be undertaken by the Council of the Chemical Society. (2) The details of administration to be conducted by "a Board of Fellows (of the Society), so selected by the Council as to be representative of all classes of chemists." (3) The benefit not to be limited to investigators and exponents of chemical science, or to Fellows of the Society, but to be open to anyone of whom it could be said, "that he is *bona fide* a chemist and is in distress." (4) The main purpose to be "the permanent relief of distressed chemists or their widows," and its aim to be "to provide annual pensions . . . . to approved applicants of a given age." (5) The selection from among these approved applicants to be "by votes (of subscribers), under which only the fittest for relief will be relieved,"—a mode represented to be the only practicable one for the distribution and sustenation of a competitive pension fund, framed as contemplated, on the lines of the Benevolent Fund of the Pharmaceutical Society.

5. Your Committee have grave doubts whether such a system of competitive annuities, under which, on an annuity becoming publicly announced as vacant, the successful applicant would secure, it might be, an undue measure of relief, while other scarcely, if at all, less deserving applicants might receive no relief at all, is a judicious or even defensible system. They consider a far more desirable plan to be that of entrusting a select body of administrators to deal privately with every case as it is brought to their notice, either by pension or otherwise, according to the circumstances of the particular case; and as regards any surplus of yearly income, either to add it to the capital fund, or let it be available for the requirements of after years, so as to make provision against the occurrence of occasional cases of urgency.

6. But whatever may be thought of these alternative modes of administering a Benevolent Fund, and putting aside for the moment the question both of the advisability or otherwise of the institution *by the Chemical Society* of any Benevolent Fund at all, and of the legal difficulties which the institution of such a Fund would have to encounter, your Committee are unhesitatingly of opinion that the administration of any fund instituted by the Chemical Society ought to be wholly unfettered by conditions imposed from without, and be conducted solely according to regulations approved and authorised by the Society itself from time to time.

7. Your Committee, while recognising that, under the Charter of the Chemical Society, the creation or acceptance of a Benevolent Fund by the Society would be attended with serious difficulty, have little doubt but that if the institution of the Fund were felt to be eminently desirable, this difficulty might, in some way or other, be obviated or overcome. But taking into account all the circumstances, and especially the considerations stated below, they question very much whether the resulting advantages would not be more than counterbalanced by the disadvantages attendant on the institution and administration of any such Fund by the Society.

8. As sustaining their doubts on this point, your Committee feel that, to whatever extent Prof. Attfield's, or some other like, Fund is, or might be, intended to afford relief to persons whose claim would be based in any way on the contributions they had made to the advancement of chemical science, the necessities of such persons are met in very full measure by the Scientific Relief Fund of the Royal Society; and that, so far as this class of persons is concerned, the effect of the institution of a distinct Relief Fund by the Chemical Society would be, *pro tanto*, to liberate the existing Royal Society Fund from its present obligations towards necessitous scientific chemists and their families, and thereby to withhold from this class of persons in the future the ready and very liberal support from that Fund which has heretofore been accorded them.

9. On the other hand, as regards the large and often poorly remunerated class of persons whose claim to relief from the proposed new Fund would be based, not on their contributions to chemical science, but on the circumstance of their having been, in different grades, honourably and usefully engaged in the practice of professional chemistry, your Committee cannot but bear in mind that the Chemical Society, though founded mainly by professional chemists, was not founded for any professional object, but solely for the advancement of the science of chemistry; and that the Society, from its origin until the present day, while sympathising with the actively progressing development of professional chemistry, and with the measures taken of late for its better recognition, has consistently declined to regard the interest of professional chemists as one with which it was especially concerned, or for which it could accept any responsibility. This being so, it would, in the opinion of your Committee, be unwise for the Society to abandon, and to lay itself open to the imputation of

* Report of a Committee of the Council of the Chemical Society.

having been ready at once to abandon, its settled and well recognised policy, as soon as it became a question of acquiring funds for the Council of the Society to control and, directly or indirectly, administer.

10. Having regard to the objects for which the Chemical Society was instituted and incorporated, it is clear that the management of its affairs must be *mainly* in the hands of the most active and distinguished of the workers in chemical science; and it appears to your Committee that the privately conducted administration by the Council of the Society, or any delegacy appointed by, and responsible to, the so constituted Council, of a Fund to be shared in common by one set of persons whose claim would be based on their contributions to chemical science, and by another and larger set of persons whose claim would be based on their engagement in chemical practice, could scarcely fail to provoke a well-founded dissatisfaction among the latter class; while a resort to any form of popular election or control would as certainly be prejudicial to persons of the former class, whose interests the Chemical Society is more especially under obligation to shield and have regard for.

11. On these grounds then, namely, the sufficiency on the one hand of the continuously increasing Scientific Relief Fund of the Royal Society to meet the distresses of persons engaged in the advancement of chemical science, and the unfitness, on the other hand, of the Chemical Society to undertake the responsibility of providing for the distresses of persons engaged in chemical practice, as well as on the legal difficulty to be got over, and on yet other grounds, which, though felt to be of importance, it has not been thought necessary to dwell on, your Committee have reluctantly come to the conclusion that they cannot recommend the Council to undertake the charge with which it has been proposed to entrust them as representing the Chemical Society, of founding and administering a "Chemists' Benevolent Fund."

Signed on behalf of the Committee,

F. A. Abel.

January 29, 1892.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending February 29th, 1892.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To General A. De Courcy Scott, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, March 14th, 1892.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 175 samples examined were found to be clear, bright, and efficiently filtered.

In other respects, also, the condition of the water supply during the month of February was throughout entirely satisfactory. In the case of the Lea-derived water supplied by the East London Company, the mean amount of organic carbon was found to be only 0·125 part, and the maximum amount 0·157 part in 100,000 parts of the water. In the case of the Thames-derived supply, the mean amount of organic carbon was only 0·137 part, and the maximum in any single sample examined 0·151 part in 100,000 parts of the water; as against a mean of 0·158 part, and maxima of 0·189 and 0·204 part in the previous month's supply.

We are, Sir,

Your obedient Servants,

William Crookes.
William Odling.
C. Meymott Tidy.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg.

Paper II.—*Analyses of Raw Materials. Preparation of Crucibles.*

The following tables show that the Poutiloff Works were in a favourable position to start the crucible steel business:—

(*a*) *Swedish Cast-iron.*	Per cent.
Carbon	3·800
Graphite	1·380
Manganese	1·040
Phosphorus	0·019
Silicon	0·728
Sulphur	0·025

(*b*) *Swedish Iron, Y.M.*	Per cent.
Carbon	0·020
Graphite	none
Manganese	0·070
Phosphorus	0·014
Silicon	0·003
Sulphur	0·014

(*c*) *Blister Steel, W.F.*	Per cent.
No. I.	
Carbon (total)	1·200
Phosphorus	1·020
Sulphur	0·015
No. II.	
Carbon (total)	1·050
Phosphorus	0·024
Sulphur	0·015
No. III.	
Carbon (total)	0·850
Phosphorus	0·020
Sulphur	0·015

(*d*) *Russian Puddled Steel.*	Per cent.
No. I.	
Carbon (total)	0·370
Phosphorus	0·022
Silicon	0·110
No. II.	
Carbon (total)	0·310
Phosphorus	0·046
Silicon	0·150
No. III.	
Carbon (total)	0·255
Phosphorus	0·030
Silicon	0·150

The Russian puddled steel (Beloretz Works) contained only traces of sulphur and manganese. We classified the blister steel and the puddled as ordinarily by the aspect of the fracture.

(*e*) *Siemens-Martin Steel.*	Per cent.
Acid.	
Carbon	0·450
Manganese	0·985
Phosphorus	0·062
Sulphur	0·027
Basic.	
Carbon	0·090
Manganese	0·440
Phosphorus	0·040
Sulphur	0·022

(*f*) *Old Crucible Steel.*	Per cent.
No. I.	
Carbon	0·958
Sulphur	0·068
Phosphorus	0·042
No. II. (*mostly files*).	
Carbon	1·082
Sulphur	0·071
Phosphorus	0·075

(*g*) *Ferromanganese.*

	Per cent.
Carbon (total)	4·020
Manganese	74·710
Phosphorus	0·077
Sulphur	0·880

(*h*) *Silicon Pig-iron.*

	Per cent.
Carbon (total)	2·930
Manganese	14·940
Silicon	10·420

The silico-spiegel (*h*) contained 10 per cent of silicon and 20 per cent of manganese.

In some cases (casting ingots for tyres) we added a certain quantity of ferrochrome. Steels containing about 0·35 per cent of chromium have a greater tenacity.

Ferrochrome from Boucau (France).

Chromium	49·25 per cent.
Carbon (total)	9·03 ,,
Aluminium	2·28 ,,
Manganese	0·70 ,,
Silicon	0·62 ,,
Phosphorus	0·08 ,,
Sulphur	0·03 ,,

Several boxes contained 60 per cent of chromium; in this alloy 11·03 per cent of carbon (total) was found.

We prepared the crucibles out of Russian fire clay, coming from the Government of Novgorod. The price was 25 paper copecks, delivered at the Works. The only foreign material used in the manufacture of crucibles was the Ceylon graphite, costing here 5·50 paper roubles. It is impossible to use the Siberian graphite owing to the enormous amount of ash it contains. A certain quantity of fire-clay was roasted. All the materials were ground up. Each crucible weighed about 50—55 pounds. The composition of the mixture for the preparation of crucibles was as follows:—

Fire-clay	43·5 per cent.
Burnt clay	36·5 ,,
Old crucibles	11·0 ,,
Graphite	9·0 ,,

The materials were mixed in a wooden tray lined with sheet iron by means of bare-footed workmen, who sprinkled the materials from time to time with water.

Composition of Raw Fire-clay.

Silica	50·00 per cent.
Alumina	47·00 ,,
Magnesia	0·46 ,,
Lime (CaO)	0·52 ,,
Alkalies	0·71 ,,
Ferric oxide	2·05 ,,

This clay is of a good quality and very seldom contains pyrites, which are easily picked out before the grinding operation commences. The burnt clay is prepared in ordinary round brick furnaces.

The mass for crucibles, formed into rough blocks, is placed for a week into a cool place and next made into crucibles in hand-moulds by driving a pestle through the mass with a wooden mallet. Two men were employed (head workman receiving 12 copecks for each crucible, and paying himself his assistant). They made 65—70 crucibles per day. After remaining about a week in the moulding room, the crucibles were removed to the drying room, at a temperature of 40—45° C., where they remained for six to eight weeks.

The crucibles stood very fairly four heats while melting hard steel, and three heats for medium steel (tyres, steel castings, &c.). The whole cost of a crucible with the cover was 1·50 roubles to the Works themselves.

Royal Institution.—Dr. B. W. Richardson will deliver his Friday Evening Discourse on "The Physiology of Dreams" on the 29th of April in place of Dr. William Huggins, who will give his lecture on "The New Star in Auriga" on the 13th of May.

NEW SEPARATION OF ZINC AND MANGANESE.

By PAUL JANNASCH and ROB. NIEDERHOFHEIM.

Recently one of the writers, in concert with J. Franzek, made known a new method for the separation of manganese, cobalt, and nickel, depending upon the precipitability of manganese from a basic potassic solution of the double cyanides of the metals concerned whilst cobalt and nickel remain in solution.

This process has now been applied with equal success to the separation of manganese and zinc. In absolute accuracy it is by no means inferior to the older process (precipitation of the manganese in a strong solution of ammonium chloride and ammonia), and is at once simple and expeditious in its performance.

0·5 grm. each of manganese and zinc sulphates are dissolved in 50 c.c. of water in a large platinum dish provided with a lip, and mixed with 10 c.c. of a 10 per cent solution of potassium cyanide, after which 10 c.c. of a 25 per cent potassa-lye are added, and the mixture is stirred with a platinum solution until the precipitate is almost entirely re-dissolved. The manganese is then precipitated with 50—60 c.c. of a pure solution of hydrogen peroxide, and the mixture (covered) is heated for 15—20 minutes upon a boiling water-bath, and then filtered into a second capacious platinum capsule and washed out with hot water. When the filtrate is quite cold it is supersaturated with hydrochloric acid (30 c.c. of the concentrated acid), and poured back into a capsule of Berlin porcelain (on account of the potassium nitrate often found in no small proportion in commercial hydrogen peroxide), evaporated to dryness, the residue heated in the air-bath to from 110°—115° for at least half an hour, re-dissolved in water with the addition of 15—20 drops of dilute hydrochloric acid, and separated by filtration from the deposiit of silica which is rarely absent. Lastly, the filtrate whilst boiling is precipitated in the prescribed manner with sodium carbonate, and the zinc is subsequently weighed as oxide. The zinc oxide, after ignition, should give a clear solution in dilute acetic acid. An insoluble residue, if present, consists of silica or alumina or of both these impurities, the latter of which appears almost regularly,—often, indeed, in considerable quantities, if the alkaline solution, manganese hydroperoxide, has been heated for a long time on the water-bath, not in a capsule of platinum, but in a porcelain vessel. As a matter of course in this method of separation the use of impure reagents which contain alumina, silica, &c., is excluded. It must further be considered that the precipitate of manganese after washing with hot water, may easily include some potassa which cannot be readily removed by ignition with the blast. It is therefore prudent to re-dissolve the precipitate in dilute nitric acid in presence of a small quantity of oxalic acid (not more than 0·3 grm.), and to re-precipitate of the manganese with hydrogen peroxide in an ammoniacal solution.

The authors hope shortly to report on further quantitative determinations and separations by means of hydrogen peroxide. At present they are engaged upon the separations of copper and zinc, copper and nickel, lead and zinc, as also bismuth and zinc. The foundations of the methods have already been ascertained, and merely require a more minute elaboration.

In particular, as regards the behaviour of copper with hydrogen peroxide, it must be mentioned that slightly ammoniacal solutions of copper containing only small quantities of ammoniacal salts are completely precipitated by an excess of hydrogen peroxide, so that in the filtrates not the slightest trace of copper is indicated by hydrogen peroxide. These precipitates are of a dark greyish green, and retain their colour even after prolonged boiling.

The alkaline solutions of the double copper cyanides are also precipitated after prolonged boiling with hydrogen peroxide, whilst many other metals remain in solution.

The authors are now engaged with the study of these reactions so important for quantitative analysis.—*Ber. der Deutsch. Chem. Gesell.*, vol. xxiv., p. 3945.

THE CHEMICAL WORKS OF FARADAY IN RELATION TO MODERN SCIENCE.*

By Prof. DEWAR, M.A., F.R.S.

Prof. Dewar commenced his lecture by saying that his eminent colleague had done such ample justice to the physical side of Faraday's work, that his own task would be limited to dealing with those early researches in which he developed that astounding manipulative power which enabled him to conduct his subsequent electrical investigations in so remarkable a manner. He proposed to give a brief sketch of the more important of the distinctive chemical labours of Faraday, and then to select one of the many veins of investigation he had opened up, and show what had resulted from its development.

Faraday's chemical work might be divided into the following groups or periods:—Period of Analytic Work. Organic Research. Study of Gaseous Properties. Investigations on Steel and Glass. Determination of Electro-chemical Equivalents. Regelation. Action of Metals on Light. Work on Chemical Manipulation. Published Lectures.

Having given a short résumé of Faraday's progress through these subjects, Prof. Dewar referred to his first great work in organic research, the production of two compounds of chlorine and carbon, the perchloride and the protochloride, and the determination of the composition of "Julian's chloride of carbon." The original specimens prepared by Faraday were exhibited, and it was pointed out that the discoverer's analyses of these bodies were absolutely accurate, notwithstanding the difficulties attending such work at that time. His discovery of "bicarburet of hydrogen" (now widely known and largely manufactured as benzol) and a "new hydrocarbon" (now known as butylene) was then described, it being pointed out that having regard to the methods of working which Faraday had to employ, the isolation and determination of the composition of such bodies was marvellous, and was to be explained only by his wonderful manipulative skill.

Probably Faraday's most remarkable discovery in organic chemistry was the fact that naphthalene could be dissolved by strong sulphuric acid, and that when thus dissolved the solution did not precipitate naphthalene on being treated with water. That enabled him to prove combination between sulphuric acid and a hydrocarbon. The body, which he called "sulpho-naphthalic acid," is probably the first of the sulpho-acids now so largely employed in the colour industry.

Faraday's next important work was an investigation into the properties of combinations of steel with other metals, in the course of which he demonstrated the now well-recognised fact that an admixture of such minute prrportions as 1-500th of such metals as silver, nickel, palladium, &c., will entirely alter the character of the metal. Concurrently with this, he worked on the improvement of optical glass, and it was observed that although the fruits of his labours in this direction lay dormant for some time, they ultimately resulted in one of his most important discoveries, namely, the rotation of the plane of polarisation in the magnetic field. The glass produced by Faraday by the fusion of oxide of lead with boracic acid was selected by him because of its superior fluidity, combined with great density. (Experiments were given illustrating the peculiar physical and electrical properties of the Faraday glass).

The next research was that on the liquefaction of gases, which, although carried out by Faraday, was nevertheless done at the instigation of Davy. Davy had discovered a substance which proved to be a hydrate of chlorine, and which he found could be kept either in ice or in sealed tubes. Faraday had produced a quantity of this substance during the cold weather, and had made an analysis of it. Davy then suggested that it should be heated in a sealed tube, and, without saying what he really expected to take place, indicated that one of three things would happen, namely, that it would either melt, act on water, or produce liquid chlorine. The latter event happened, and opened up vast possibilities, the prosecution of which Davy left to Faraday. (Experiment on the liquefaction of chlorine given). The necessity of obtaining tubes strong enough to stand the pressure required for the liquefaction experiments led Faraday to make investigations at this time into the production of bottle and other glass.

Faraday next turned his attention to researches on the electro-chemical relations of bodies, crystallisation, and the action of metals on light. It was in connection with the research on crystallisation in 1856 that Faraday made his interesting discovery of the phenomenon of regelation, by virtue of which two portions of a piece of ice, after being severed, freeze together again on being brought into contact, even when the temperature of the surrounding medium is higher than the freezing-point of water. Although discovered by Faraday, it was not until comparatively recent times that the explanation of the phenomenon was given and its influence on glacial motion clearly established. (Experiment on regelation shown).

Specimens, arranged and tabulated by himself, of Faraday's last research on the optical properties of gold leaf in a highly attenuated form were exhibited and described.

Turning then to the special subject of the evening's discourse, the liquefaction of gases, Prof. Dewar stated that although Faraday made his first researches in this direction as early as 1823, the matter lay dormant for many years, until his interest in it was re-awakened by Thilorier's discovery that solid carbonic acid could be produced in the form of a snow-like substance, boiling at −80° C., and capable of being handled. Faraday was the first to introduce this discovery into England in a lecture given at the Royal Institution on the 18th May, 1838, and thereafter by its aid he resumed his work on the liquefaction of the various gases which had resisted his former efforts. All through the summer of 1844 he was busily employed at this work, using the low temperatures, which Thilorier's new product enabled him to obtain, combined with great pressures. (Specimens of gases thus liquefied by Faraday shown). This important work was the subject of a Friday evening lecture given at the Royal Institution early in 1845, a full abstract of which appeared in the *Times* of that date, the Institution itself not having then commenced the publication of its proceedings. In the course of that Address Faraday produced a small quantity of ethylene, and he expressed the opinion that if a method could be found of producing liquid nitrous oxide in large quantities, that would be the material which would enable him to liquefy oxygen and the other gases which had hitherto resisted all his efforts. (Experiments showing the comparative boiling-points of solid carbonic acid, nitrous oxide, and ethylene at ordinary pressure and under diminished pressure given). Faraday hoped that the production of solid nitrous oxide would enable him to get temperatures as far below the boiling-point of carbonic acid as the temperature of that body was below ordinary temperatures. As a matter of fact, it is impossible to reach such low temperatures by the agency of solid nitrous oxide, and such great depression of temperature was not attained until such time as liquid ethylene became available. The lecturer here showed and described a diagram of the machinery and apparatus now employed at the Royal Institution for the liquefaction

* An Address delivered at the Faraday Centenary, Royal Institution of Great Britain, Friday, June 26, 1891.

and solidification of gases. The method of producing liquid ethylene and of employing it over and over again in the apparatus was described.

The work done in connection with this subject since the time of Faraday, and especially the investigations of Andrews and Van der Waals, had enabled scientists of the present day to calculate exactly the temperature of the boiling-point of hydrogen, the gaseous body which has in the liquid state the lowest boiling-point of all the elementary substances, and which has up to the present time resisted liquefaction. The temperature of boiling hydrogen would be −250° C. The lowest point attained by Faraday was 110° C., and the lowest temperature yet reached was −210° C.

Prof. Dewar then performed the experiment of actually producing liquid oxygen, which was seen to boil quietly when collected in an open vessel at a temperature of −180° C. The colour was slightly blue, only a few particles of solid matter being visible, which Prof. Dewar explained were traces of solid carbonic acid, the elimination of which had given him considerable trouble. The lecturer further proved by actual experiment on his own hand and on a glass vessel that the liquid oxygen was in the spheroidal condition; and also that alcohol when added to the liquid became instantly solidified. The usual test for oxygen by means of a glowing taper was also made on the vapour given off by the liquid.

Prof. Dewar stated that the prosecution of the researches inaugurated by Faraday was enabling scientists to approach nearer and nearer to the zero of absolute temperature; and the speculations of physicists were now directed to the probable characteristics of hydrogen and of matter in general when that condition should be attained. At such a temperature the properties of matter would in all probability be entirely changed; the old Lucretian law would be suspended, molecular motion would probably cease, and what might be called the death of matter would ensue—as in fact the death of chemical affinity and chemical action was known to take place at the low temperatures already attainable. (Experiment proving this by the immersion of phosphorus, sodium, and potassium in liquid oxygen). On the other hand, it was found that even at such low temperatures oxygen retained its characteristic absorption spectrum.* Further experiments were given proving the liquefaction of ozone by means of liquid oxygen—a tube of the liquid thus produced showing the characteristic deep blue colour of that substance.

In conclusion, Prof. Dewar said that although great progress had been made since Faraday's time, chemists were still working distinctly on the lines of his early researches, and it seemed to him that no fitter method of celebrating the centenary of Faraday's birth could be chosen than the demonstration of the realisation of some of his own ideas.

On the conclusion of the lecture, a vote of thanks to Prof. Dewar was moved by the LORD CHANCELLOR, who said:—

My Lord Duke, my Lords, Ladies, and Gentlemen,—I am very happy indeed to be made the instrument of conveying your thanks for the most interesting lecture we have listened to. I could not help thinking while our lecturer was giving us an account of all these wonderful things, that he was illustrating in his own person something which he had said. He pointed out how the torch of science was passed on from hand to hand: how, for instance, Davy had handed to Faraday some of the sources of those great discoveries which he afterwards disclosed to the world; and I thought that it required some such successor to give adequate expression to the history of Faraday's work. Faraday had many friends; many of us have listened to him in this theatre, as, indeed, I have had the privilege of doing myself; and I think I may say that no one came within the sphere of his kindly and gentle influence who did not become a hearty and attached friend. But I should think that very few of those friends would be able to give adequate expression to what he had done, the discoveries he had made, and the ever increasing effect which those discoveries had exercised upon the progress of modern science. We have listened to-night to a most able exposition of Faraday's work, and I think that Prof. Dewar has shown that he has in truth succeeded to that work, that he is worthy to receive that torch, and carry it on and give a brighter illumination to science than it has ever yet received. I am sure that there is none here who will not heartily join with your Grace in thanking Prof. Dewar for the able, learned, and lucid lecture in which he has explained to ignorant people like myself Faraday's wonderful discoveries in science.

Sir LYON PLAYFAIR, in seconding the motion, said:—It is indeed a great privilege to all of us to see the great progress which has been made in the discoveries of Faraday during the last fifty years. Those little tubes containing the original liquefied gases which Faraday liquefied under pressure and low temperatures were very important, and were considered at the time very remarkable productions. But you see how the subject has since grown; how carbonic acid, for instance, first liquefied, has since been solidified so that it can be handled like snow; and you have seen the remarkable way in which oxygen has been liquefied on the present occasion. An old Professor of chemistry like myself can appreciate the wonderful manipulative power which Prof. Dewar has displayed this evening. Even in the chemical laboratory, with everything quiet around you, it is difficult to make these experiments successfully, but in a theatre of this kind it is marvellous how everything goes wrong; and if we had not had a manipulator of great accuracy and knowledge, we could not have had the gratification which we have enjoyed this evening. What strikes me as being so excellent in my friend, and much more than friend,—for he is the greatest chemist that I ever produced,—and I am extremely glad to think that he looks up to his old teacher with affection while I look to him with love and honour—what I wanted to say is, that I think he has done quite rightly in giving you the scientific side of these wonderful discoveries, and showing you the way in which they are growing and giving us a better knowledge of the condition of matter. When Faraday first made experiments like these, some wiseacres said, What is the use of it? Faraday replied, "Will you tell me what is the use of a baby?" But Faraday's baby has centred around it all the hopes and desires of the parents that produced it, and the State also has shown much interest in its upbringing. The bodies that appear in those tubes have become important factors in the progress and industry of the world. The carbonic acid, which I recollect first seeing as a little globule of acid, is now carried in cylinders filling railway trucks, and is applied to many purposes, some important, others more useful than important. For instance, the liquid carbonic acid enables barmaids to get beer up from the cellars below without pumping it; that nitrous oxide which we were so interested in as a con-

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* The recently discovered magnetic property of the liquid adds a new interest to this substance.

"Royal Institution, 10th December, 1891.

"DEAR SIR WILLIAM THOMSON,—The following observation, which I have just made, may interest the members of the Royal Society, and if you think it of sufficient importance you may announce it at this day's meeting.

"At 3 p.m. this afternoon I placed a quantity of liquid oxygen in the state of rapid ebullition in air (and therefore at a temperature of −182° C.) between the poles of the historic Faraday magnet, in a cup-shaped piece of rock salt (which I have found is not moistened by liquid oxygen, and therefore keeps it in the spheroidal state), and to my surprise I have witnessed the liquid oxygen, as soon as the magnet was stimulated, *suddenly leap up to the poles and remain there permanently attached until it evaporated.* To see liquid oxygen suddenly attracted by the magnet is a very beautiful confirmation of our knowledge of the properties of gaseous oxygen.—Yours faithfully, JAMES DEWAR."—*Proc. Roy. Soc.*, vol. i., p. 24.

densed gas is now largely used by dentists as a means of extracting our teeth without pain; sulphurous acid will, I am certain, become most important in war, for if you took a brittle shell filled with liquid sulphurous acid and threw it between the decks of a ship it would produce such a stink that everybody would disappear in a moment. The time is coming when other gases will be used in this way. Their importance does not altogether consist in their applications to industry, though they are becoming very important in that way. But their importance is that they are teaching us more of the constitution and properties of matter; it is in that respect that they are becoming so interesting in the eyes of scientific men. I have been extremely interested in watching the production of that liquid oxygen. I looked upon it with great respect and wondered to see it not covered with a cage as if likely to go off at any moment in a terrific explosion. But it is produced in such a manner that its own cold keeps it down, and so we saw it handled in the most marvellous way as an ordinary liquid. I have the utmost pleasure in seconding the vote of thanks to Prof. Dewar for the brilliant exposition which he has given us.

The Chairman then put the motion, and it was carried with acclamation.

Prof. Dewar, in reply, said: My Lord Duke, my Lords, Ladies, and Gentlemen,—I am exceedingly indebted to you for the very kind way in which you have referred to the labours of the lecturer. I can assure you that it has been a source of great pleasure to me, and that in fact I have had the least part to do. This kind of illustration cannot possibly be given without means of various kinds, and there are several benefactors whom I should like to mention in connection with this lecture. First of all, Dr. Anderson gave the pumps which enabled me to compress and evaporate such volatile bodies; secondly, we require machinery to set those pumps in motion, and somebody to look after it, and that has been supplied by the kindness of Mr. Robert Wilson, of the well-known firm of Messrs. Crossley, who is always ready and willing to help us; thirdly, as regards the cost of the material used—which has been by no means small—I am indebted to another member and great benefactor of the Institution, namely, Mr. Ludwig Mond, F.R.S. And lastly, but not least, I am indebted to my assistants, Mr. Lennox and Mr. Heath, for the assiduous and self-sacrificing way in which they have laboured in order to make these experiments go successfully. As Sir Lyon Playfair has said, it is comparatively easy to do these things in the quiet of the laboratory, but immensely difficult to get them to go on an occasion like this; and when we consider the long distances over which these highly condensed gases have to be conveyed, and the complex arrangements necessary to avoid all fear of danger, I think you will agree that the benefactors who rendered these arrangements possible are deserving of more credit than the lecturer.

Lord Justice Fry then proposed a vote of thanks to his Grace the Duke of Northumberland for his kindness in presiding over the meeting. In doing so his Lordship said: While I ask you to tender his Grace your hearty thanks for attending to-night, I cannot omit to ask you to thank him also for even greater services. He has presided over this Institution for many years, and has ever shown in its affairs a warm and intelligent interest, and he has been a most liberal benefactor of the Institution. At our ordinary meetings we have no opportunity of expressing our feelings to our benefactors, but on this extraordinary occasion we have that opportunity. I feel that I only express the sentiments of all here when I propose to proffer your warmest thanks to his Grace, not only for presiding this evening, but also for the great debt of gratitute which we owe him for his past services.

Sir Richard Webster said: I have the great privilege of being permitted to second the vote of thanks to his Grace. I most heartily endorse all that Lord Justice Fry has said with respect to the eminent services rendered to this Institution by his Grace the Chairman. I also heartily agree with what has been said by previous speakers with respect to the admirable lecture that we have heard to-night, some portion of which will, I hope, remain in my mind and memory, but the immediate effect of which has been to completely paralyse the power of ordinary speech. I feel it a great privilege to have been permitted to take some part in the proceedings, and have the greatest pleasure in seconding the vote proposed by Lord Justice Fry, which I venture to hope may be carried by acclamation.

The vote having been put and carried by acclamation,

The Duke of Northumberland said in response: My Lords, Ladies, and Gentlemen, I feel somewhat embarrassed on the present occasion, because I had no expectation of, nor did I feel myself entitled to, the vote of thanks you have been so kind as to pass. I should have been wanting in duty if I had not been here to attend the Centenary of the illustrious man whose memory we have met to celebrate; and I must say I have been amply rewarded by the lectures I have heard, both from Lord Rayleigh and Prof. Dewar. They have almost persuaded me between them that I understand something of this science, which I confess but for them would have seemed impossible. Time is getting on, and I therefore will not detain you longer than to thank you most sincerely, and to ask you to accept this simple expression of my gratitude.

ON THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILISERS CONTAINING COTTON-SEED MEAL.*

By F. B. Dancy, A.B.

The term *available* phosphoric acid is used to denote the difference between the *total* phosphoric acid in a fertiliser and the *insoluble*. The *total* phosphoric acid is the entire amount of phosphoric acid, of whatever kind, that the fertiliser contains. The *insoluble* phosphoric acid is, as generally accepted, that phosphoric acid which is left after 2 grms. of the fertiliser, ground to pass a sieve of approximately 20 meshes to the linear inch, have had the *soluble* phosphoric acid extracted with cold water and then been digested for thirty minutes, with agitation every five minutes, at 65° C., with 100 c.c. of a strictly neutral solution of ammonium citrate of a specific gravity of 1·09, immediately after which digestion they have been thoroughly washed with cold water.

The *available*, then, being the difference between the *total* and the *insoluble*, it follows that *insolubles* being equal, the *available* varies exactly and directly as the *total*, and *totals* being equal, the *available* varies exactly, though inversely, as the *insoluble*.

The *total* is a definite and fixed quantity, and there should, therefore, be no material variation in its determination between the work of accurate analysts. Not so with the others. The *soluble*, *insoluble*, *reverted*, and *available* are not fixed and definite quantities: they are dependent on so many conditions of time, temperature, degree of fineness, quality and quantity of solvent, agitation, &c., that it is no matter of wonder that even skilful manipulators vary in their determination. They are the results of methods, and will vary according to the method or manner of executing the details of the method. But, as has been remarked, and as its name implies, the *total* is *all* the phosphoric acid in the material under examination, of whatever kind and in whatever shape or form. It is not what is gotten by a method, but *what there is there*, and any method, therefore, that fails to reach any part or kind of it is not a method for *total* phosphoric acid. It is

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

sometimes said that discrimination is impracticable, and that all fertilisers should be treated equally and alike. The position is untenable. It might as well be urged that in order not to discriminate, the plain soda-lime method for the determination of nitrogen should be used on all fertilisers, those containing nitrates as well as those containing organic nitrogen alone, when everyone knows that it is inadequate in the presence of nitrates. So a *total* method which is adequate for some kinds of fertilisers, but not for others, cannot be applied to all on the above ground or any other ground without manifest injustice to those fertilisers for which the method is inadequate.

The Association of Official Agricultural Chemists in their official methods ("Bulletin 24, United States Department of Agriculture"), give three alternate methods of determining *total* phosphoric acid. There is no distinction made between them, no indication that either is better adapted than the other for any particular class of fertilisers. The presumption is that they are given as interchangeable and equally allowable for all classes of fertilisers at the pleasure or option of the operator. It is the purpose of this article to show that one of them at least is entirely inadequate for fertilisers that contain cotton-seed meal, and that any chemist who uses this method on such fertilisers is in almost certain danger of doing these fertilisers a great injustice. The method referred to is the second of the three given, namely, "Solution in 30 c.c. of concentrated nitric acid with a small quantity of hydrochloric acid." The writer has not extended his investigation, except imperfectly, to the other two methods. It is only with this one, as applied to cotton-seed fertilisers, that this article has to do.

Cotton-seed fertilisers are comparatively unknown in the North. It seems, therefore, that the Southern members of the Association of Official Agricultural Chemists could not have been very wide awake to the interests of a class of fertiliser manufacturers peculiar to their own section of country when they failed to have attached to this method, at the time when it was adopted by their association as one of three alternate methods, the limitation "not applicable to fertilisers containing cotton-seed meal."

Cotton-seed meal is readily and entirely soluble in either "nitric acid with a small quantity of hydrochloric acid" or in nitric acid alone. *But such a solution does not give up its phosphoric acid to molybdic solution.* It would appear that certain nitro-organic compounds are formed which prevent the phosphoric acid in the solution from being yielded up to the molybdic precipitant. Whether this is affected by in some way rendering the menstruum a solvent for the phospho-molybdate of ammonia that ought to be formed, or, by holding the phosphoric acid in check, thus preventing such a combination, is not clear. But the fact remains. The attention of the writer was first forcibly directed to it when a sample of cotton-seed meal was submitted to him for a determination of the *available* phosphoric acid it contained. A nitric acid solution of 2 grms. of it was made (using also a little hydrochloric acid), the solution being perfect, and a total phosphoric acid percentage of 0·51 found. A duplicate made in the same way yielded 0·54 per cent. Being convinced that there was much more phosphoric acid in the meal than this, and recalling that a short time previously a gentleman had remarked that a friend of his had found materially more phosphoric acid in the ash of cotton-seed meal than by acid solution, 2 grms. of the meal were ignited to perfect ash, the ash dissolved in acid, and a percentage of 3·24 of *total* phosphoric acid found; a duplicate in the same manner yielded 3·20, though in this case the incineration was not quite so perfect, a little char being left. The true per cent of *total* phosphoric acid in the meal then was 3·24. A solution of 2 grms. made by hydrochloric acid with chlorate of potash also failed by something more than half of getting the full amount. This yielded 1·45 per cent. Next 2 grms. of the meal were taken, washed with cold water in exactly the same manner as when extracting *soluble* phosphoric acid from an ordinary fertiliser, then digested with citrate solution, and again washed exactly as is done in the determination of *insoluble* phosphoric acid. The residue was ignited and the phosphoric acid determined. It was found to be 0·24 per cent. So not only did a cotton-seed meal, which showed only half a per cent of *total* phosphoric acid to a nitric acid solution, contain in reality 3¼ per cent, but 3 per cent of this 3¼ per cent was *available* by the methods of analysis.

A cotton-seed meal fertiliser may easily contain one-third cotton-seed meal, and, if the meal had the composition of that examined above, would owe 1 per cent of its *available* phosphoric acid to the meal. If, therefore, such a fertiliser were to be analysed by the nitric acid method, it would theoretically show a shortage of nearly 1 per cent of *available* phosphoric acid (0·90 exactly). While none of the experiments herein given exhibit as great a disparity as this, some approximate it, and it is believed that a disparity fully equal to this is quite possible. Whether the entire disparity is always due to the retention of the phosphoric acid of the meal alone, or whether in some cases the meal, while holding some of the phosphoric acid of the phosphate in check gives up more of its own, or whether, in other cases, the phosphoric acid of the phosphate in precipitating carries more of the meal's phosphoric acid down with it than would otherwise go, and thus lessens the disparity, is not clear. I am inclined to think that new and fresh meal will exhibit this peculiarity in a greater degree than old meal, though of that I cannot speak definitely. However that may be, there seems to be not much doubt that the disparity will be greater or less according to various conditions not well understood, and may vary from a third or a half of a per cent to even as much as 1 per cent.

Six fertilisers containing cotton-seed meal were chosen. They were not laboratory mixtures, but bona fide commercial fertilisers on sale in North Carolina. They will be distinguished as 56, 76, 77, 78, 110, and 57. In each the phosphoric acid was determined by dissolving 2 grms. in nitric acid plus a little hydrochloric acid with protracted heating. This is designated in the table below as "acid solution." Then in each the phosphoric acid was determined by incinerating 2 grms. and dissolving the ash in nitric acid. This is designated in the table as "incineration." Following are the results:—

	Total phosphoric acid.					
	56.	76.	77.	78.	110.	57.
Incineration] ..	10·04	9·77	9·16	9·93	10·07	9·97
Acid solution ..	9·49	9·13	8·66	9·25	9·56	9·95
Difference ..	0·55	0·64	0·50	0·68	0·51	0·02

No. 57 was an old cotton-seed meal fertiliser that had been carried over from last season. The meal had completely changed colour to a dark brown, so that to the eye the fertiliser would never have been judged to be a cotton-seed fertiliser. In this one alone was there no difference in the results of the two methods.

(To be continued.)

Examination of the Air at Breweries, &c., for Micro-Organisms.—P. Lindner (*Wochenschrift fur Brauerei*).—The author places in every part of the establishment which appears questionable three sterilised glass cylinders side by side, leaving them uncovered for one hour. At the end of this time the first cylinder is charged with sterilised wort, the second with wort-gelatin, and the third with meat-juice gelatin, using the requisite precautions. Each cylinder is then closed with sterilised tufts of wadding, and in the two last cylinders the gelatin is caused to congeal uniformly over the sides, as in Esmarch's tube-cultures. The tube-cultures are then examined in the usual manner.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 17th, 1892.

Dr. W. J. Russell, F.R.S., Vice-President, in the Chair.

Messrs. John C. Hewlett, William Pullinger, Edward C. Cyril Baly, and John C. Chorley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Hudson Donaldson, Trevyr House, Grantham; Henry Leonard Humell, 15, Mawdsley Street, Bolton; Cressacre George Moor, B.A., St. Clement's Vicarage, Truro; John Meadows Smith, 66, College Street, Chelsea, S.W.; George de Roos Thompson, 28, Treleth Road, Askam-in-Furness, Lancashire; Arthur Holt Tuer, Thornhill, Wigan, Lancashire.

Of the following papers, those marked * were read:—

*121. "*A Study of the Conditions which Determine Combination between the Cyanides of Zinc and Mercury; and of the Composition and Properties of the Resulting Double Salt.*" By Wyndham R. Dunstan.

When a solution of zinc sulphate is added to a solution of mercuric potassium cyanide [$HgK_2(CN)_4$], or when mercuric chloride is added to a solution of zinc potassium cyanide [$ZnK_2(CN)_4$], a white precipitate is formed which has been stated, on the authority of Gmelin, to consist of a double cyanide of zinc and mercury of the formula $ZnHg(CN)_4$. This, the author has shown, is not the case (*Pharm. J.*, iii., 20, 653; *C.S. Abstr.*, 1890, 855). The precipitate loses a large quantity of mercuric cyanide when it is washed with cold water, some, however, remaining attached to the cyanide of zinc. Previous experiments seemed to point to the conclusion that the mercuric cyanide thus retained is not combined, but in some manner mechanically entangled by the zinc cyanide. This view is, however, disposed of by further experiments, of which an account is now given.

The precipitate is in many respects a remarkable substance. The amount of mercuric cyanide "retained" is dependent on the amount of water present during precipitation, as well as on the proportion in which the salts interact; the maximum quantity retained is 38·5 per cent. Zinc cyanide having this percentage of mercuric cyanide attached to it in such a form that it cannot be removed by ordinary washing with cold water is precipitated when cold saturated solutions of the two salts are mixed in equimolecular proportions. The washed precipitate is amorphous. Prolonged contact with cold water leads to the gradual removal of mercuric cyanide. Boiling water dissolves the mercuric salt more rapidly. A cold solution of potassium iodide readily dissolves the mercuric cyanide with the formation of the soluble double salt—

$$Hg(CN)_2{\cdot}2KI.$$

A series of experiments in which the masses of the interacting salts were varied proved that a compound of the two cyanides is formed, and suffers decomposition to a greater or less extent, depending on the relative amount of water present. An examination of the curves plotted from these results leads to the inference that the composition of the double salt is expressed by the formula $Zn_4Hg(CN)_{10}$, that is to say, the two cyanides are present in it in the proportion $Zn(CN)_2{,}\frac{1}{4}Hg(CN)_2$. Such a salt contains 40·6 per cent of mercuric cyanide. It cannot be obtained pure, since it is decomposed by water, and it can only be produced by precipitation of aqueous solutions. Under the most favourable circumstances, when the quantity of water present is reduced to a minimum, a substance containing 98 per cent of the double cyanide is obtained; the remaining 2 per cent consists of zinc cyanide, resulting from the decomposition of some of the double salt by water, the mercuric cyanide being dissolved, whilst the insoluble zinc cyanide remains mixed with the double salt. All attempts to prepare the double cyanide by other methods than that of precipitation have failed. Fundamental molecules of zinc cyanide and mercuric cyanide must apparently be present, in order that combination may occur. The aggregates of fundamental molecules $[Zn(CN)_2]_n$ and $[Hg(CN)_2]_n$, which constitute the solid salts, show no tendency to combine. No evidence is forthcoming of the existence of any other compound of the two cyanides than that now described. No similar compound of zinc cyanide with other metallic cyanides than that of mercury could be obtained.

This tetrazincic monomercuridecacyanide, mixed with more or less zinc cyanide, has been found by Sir Joseph Lister to be an admirable surgical antiseptic, and it is at his suggestion that the enquiry was undertaken.

A full account of the best method of preparing the salt is given in the author's previous paper.

Discussion.

Sir Joseph Lister said that the great value of the salt arose from the circumstance that while equally effective as an antiseptic, it had none of the irritant qualities of mercuric cyanide; and its slight solubility was an advantage. When mercuric chloride was used, it was liable, on the one hand, to be washed away by the discharges, and, on the other, to accumulate until a solution was formed which was so concentrated that it caused great irritation.

*122. "*A Lecture Experiment to Illustrate the Phenomena of Coal Dust Explosions.*" By T. E. Thorpe, F.R.S.

The author describes an apparatus by which the phenomena of a coal dust explosion, resulting either from a local explosion of fire-damp or by the direct action of a blown-out shot, may be illustrated. For class-room demonstration he recommends the substitution of lycopodium powder for the coal dust, on account of the greater ease and certainty of the experiment, and also because its use allows of the observance of certain phenomena, such as the mode in which the dust which escapes complete combustion is thrown on projecting objects, and also the fact that the explosion gathers strength as it progresses, which is made evident by the gradually increasing area of clear space before such objects as the dust is swept away by the force of the explosive flame.

By observations made by means of a List manometer with this apparatus, he finds that there is no evidence of a diminution of pressure along the sides of the space through which the flame rushes, and he is of opinion that there is no experimental proof of the validity of the "suction theory" held by certain colliery managers, which assumes that in consequence of this alleged diminution of pressure occluded fire-damp is drawn out from the coal, and contributes to the violence of the explosion.

Discussion.

Mr. Howard referred to two cases of "dust" explosions within his experience: one had occurred in a mill in which cinchona bark, a by no means inflammable substance, was ground; in the other case, soot produced by the burning of camphor had exploded after the fire itself had been put out.

Professor Thorpe, in reply to a question of Mr. Bevan, said that although the explosion of coal dust was doubtless influenced by its composition, the condition of the dust appeared to be the more important factor. Mr. Newth had found that charcoal powder would explode.

*123. "*The Production of the Ketone 1 : 2 : 4-Acetylorthoxylene from Camphor by the Action of Sulphuric Acid and Zinc Chloride.*" By Henry E. Armstrong and F. Stanley Kipping.

In a recent communication (*Proc. C.S.*, 1891, 188) the authors stated that they had separated from the crude

product of the action of sulphuric acid on camphor a ketone of the formula $C_9H_{12}O$, mentioning that the results obtained on analysing its hydroxime were unsatisfactory; subsequent analyses of the hydroxime and several other derivatives of the ketone have, however, all given results confirming the formula $C_9H_{12}O$.

On treatment with bromine, the ketone yields an unstable bromide which readily decomposes, yielding the monobromo-derivative, $C_9H_{11}BrO$; this latter crystallises from petroleum spirit in colourless lustrous flakes melting at 63—64°.

On oxidation with dilute nitric acid, the ketone yields two acids separable by means of chloroform. One of these proves to be paraxylic acid, *i.e.*, 1 : 2 : 4-dimethylbenzoic acid; the other being xylidinic, or 1 : 2 : 4-methylisophthalic acid. The formation of these two acids served to show that the ketone is 1 : 2 : 4-acetylorthoxylene, a compound which had already been prepared synthetically by Claus by the interaction of acetic chloride and orthoxylene in presence of aluminium chloride. The description of his product given by Claus was found to be substantially applicable to the product from camphor, but all doubt was set at rest by a direct comparison of the ketone prepared in accordance with Claus's directions with that obtained from camphor.

The theoretical bearing of this result will be fully discussed in the complete paper.

The authors are still engaged in examining the crude product contained in the ketone, in order to ascertain the nature of the constituent which communicates to it the characteristic strong peppermint-like odour which it possesses, and which appears not to be exhibited by pure acetylorthoxylene.

124. "*Platinum Tetrachloride.*" By W. PULLINGER, B.A.

The author has obtained this substance by heating hydrated hydrogen platinic chloride in a current of dry hydrogen chloride at 165° during fifteen hours. When thus prepared, it is a very soluble, but not deliquescent, substance.

125. "*Note on a New Acid from Camphoric Acid.*" By W. H. PERKIN, jun., Ph.D., F.R.S.

When warmed with sulphuric acid at 65°, camphoric acid is converted into sulphocamphoric acid with loss of water and carbon monoxide:—

$$C_{10}H_{16}O_4 + H_2SO_4 = C_9H_{16}SO_6 + CO + H_2O.$$

This remarkable decomposition was first examined by Walter (*Ann. Chim. Phys.* [3], ix., 177); subsequently by Kachler (*Annalen*, clxix., 183), and by Zepharovich (*Jahr.*, 1877, 641). Kachler showed that, when fused with potash, sulphocamphoric acid yields a crystalline substance, $C_9H_{12}O_2$ (m. p. 148°), which, although soluble in alkalis, is apparently not an acid.

In repeating Kachler's experiments, the author sulphonated camphoric acid at 100°, and fused the resulting sulphonic acid with potash, according to Kachler's directions. The resulting product was distilled under reduced pressure, and the distillate, which on cooling completely solidified, was purified by means of baryta water, and subsequent re-crystallisation from dilute acetic acid. It was thus obtained in the form of beautiful glistening prisms which melt at 108° and sublime readily at 100°. The analysis gave the following numbers:—

	Theory, $C_9H_{12}O_2$. Per cent.	Found. Per cent.
C	71·0	70·7
H	7·9	8·1

This compound, which is isomeric with that described by Kachler, is a well characterised monobasic acid. The *silver salt*, $C_9H_{11}AgO_2$, was obtained on adding silver nitrate to a neutral solution of the ammonium salt as a white crystalline precipitate, which, on analysis, gave the following numbers:—

	Theory, $C_9H_{11}AgO_2$. Per cent.	Found. Per cent.
C	41·7	41·5
H	4·3	4·4
Ag	41·7	41·8

From these results it would appear that the acid obtained by sulphonating camphoric acid at 100° is isomeric with ordinary sulphocamphoric acid. The author is engaged in an experimental comparison of these sulphoacids, and also with a detailed investigation of the new acid and of Kachler's isomeric compound.

126. "*The Specific Rotatory and Cupric Reducing Power of Invert Sugar and of Dextrose obtained from Cane Sugar by means of Invertase.*" By JAMES O'SULLIVAN.

After referring to the various values assigned to the rotatory power of lævulose and to the doubt thrown on Dubrunfaut's value by the statements of Herzfeld, Bornstein, and Winter, the author minutely describes experiments in which hydrolysis of cane sugar was effected by invertase instead of by means of acid. The conclusion finally arrived at is that, as the specific rotatory power of invert sugar obtained by means of invertase, which has no action on lævulose, is $[\alpha]_j = -24°5$, and that of the dextrose prepared from such invert sugar is $[\alpha]_j = 57°$, the apparent specific rotatory power of lævulose calculated from these numbers must be—

$$-24·5 \times 2 + 57° = [\alpha]_j - 106$$

or $[\alpha]_D - 93·8$, a value agreeing with that generally accepted.

127. "*Ethyldimethylamidobenzene.*" By W. R. HODGKINSON and LEONHARD LIMPACH.

The authors have prepared this amine by heating paraxylidine chlorhydride with ethylic alcohol under pressure at 250—300°; the product also contains diethyldimethylamidobenzene. The purification was effected by converting the mixture into sulphates; after re-crystallising the difficultly soluble sulphate of the ethyldimethylamine, the formyl compound was prepared and crystallised from weak alcohol.

The pure amine boils at 247°; its formyl derivative crystallises in long silky needles melting at 104—105°; its acetyl derivative forms brilliant prisms melting at 142—143°.

128. "*Action of Nitric Acid on Oxanilide and its Analogues.*" By A. G. PERKIN.

Although acetanilide and similar compounds are readily converted into mononitro-derivatives, the preparation of dinitro-compounds from them is often attended with difficulty, and trinitranilide has not hitherto been obtained directly from aniline or its derivatives. The author finds that oxanilide and its analogues are readily converted by nitration into the higher nitro-derivatives.

An improved method of preparing oxanilide and similar compounds is described, consisting in adding the oxalate of the amine to boiling coal tar cresylic acid and boiling the saturated solution for a few minutes.

The preparation and properties of the following substances are described:—

Tetra- and hexa-nitroxanilide.
Di- and tetra-nitroxalorthotoluide.
Tetranitroxalparatoluide.
Dinitroxal-β-naphthylide.
Tetranitroxal-α-naphthylcarbamide.
" "
Mono-, di-, and tri-nitroxanilic acids.

Higher derivatives of the toluides could not be obtained; the naphthylcarbamide derivatives were obtained as products of the continued action of nitric acid on the dinitroxalnaphthylides.

At the next meeting, on April 7th, the following papers will be read:—

"Platinous Chloride and its Use as a Source of Chlorine." By W. A. Shenstone and C. R. Beck.

"The Action of Silicon Tetrachloride on Substituted Phenylamines." By Professor Emerson Reynolds, F.R.S.

NOTICES OF BOOKS.

The Tannins. A Monograph of the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents. With an Index to the Literature of the Subject. By Henry Trimble, Ph.M., Volume I. Philadelphia: J. B. Lippincott Co., 8vo., pp. 165.

We have here the first volume of a monograph of a very complex and important department of vegetable chemistry. The author begins with an account of the early recognition of tannin as a distinct proximate principle, which he traces to the last ten years of the Eighteenth Century. Of course, astringents had been used in the arts from prehistoric ages, but without any inquiry as to their active principle. He uses the term tannin to include the whole class of astringents, and restricts the name tannic acid to the product from galls when purified.

The classification of tannins according as they form green or blue precipitates with the salts of iron is justly rejected by Mr. Trimble, since free acids, especially the tartaric, determine the green colouration, whilst, on the other hand, a cautious addition of an alkali changes the "greening" to the "blueing" tannins. As a more scientific classification he gives that proposed by Wagner, who divides tannins into the *pathological*, those produced in plants by the sting of an insect, and the *physiological*, which is generated normally in the tissues of plants.

The various methods devised for the determination of tannin are described, and the preference is awarded to that of Loewenthal, which is, however, recognised as by no means perfect.

The author concludes that tannic acid as we know it is either a glucoside of digallic acid or a mixture of this glucoside with variable proportions of digallic acid.

There is a very elaborate bibliography of the tannins which will be very useful to those studying this subject, but which we think might have been more appropriately placed in the promised second volume, after the description of the numerous astringent plants. This bibliography briefly mentions a paper on "Animal Tannin," by M. Villon, Chemical News, vol. lvi. This chemist obtained a modification of tannin from a corn-weevil. In the *Transactions* of the London Entomological Society for 1887, Mr. J. W. Slater shows the presence of tannin in a number of beetles which feed on vegetable matter.

We shall welcome the appearance of the concluding volume of Mr. Trimble's work.

Outlines of Theoretical Chemistry. By Lothar Meyer, Professor of Chemistry in the University of Tübingen. Translated by P. Phillips Bedson, D.Sc., F.C.S., and W. Carleton Williams, B.Sc., F.C.S. With a Preface by the Author. 8vo., pp. 220. London: Longmans, Green, and Co.

This work belongs to a class which is at once useful and not overcrowded. The author tells us in the special preface which he has supplied for the English edition that he has written not for students alone, but has "been desirous of offering something to those friends of scientific investigation who have neither the intention nor the time to concern themselves with the details of chemical investigation, but wish to become acquainted with the general conclusions arrived at."

In other words, he endeavours to show as far as possible the complete building without obtruding the ladders and the scaffolding upon our view. This is certainly at once the most pleasing and the most rational way of expounding the truths of chemistry to the non-specialist.

In accordance with this principle Professor L. Meyer expounds the leading conclusions of chemical science as at present recognised in a series of 123 sections, clearly written and judiciously arranged.

Concerning the capital question of the nature of the elements the author considers it improbable that they are really "primal forms of matter." He thinks that they will prove to be "combinations of units of a higher order." Prout's hypothesis he considers opposed to the best atomic weight determinations of Berzelius, Marignac, and Stas. This assertion cannot be contradicted. At the same time it might not have been useless to call attention to the fact that the atomic weights as actually determined approach in many cases curiously near to the values which they ought to present according to Prout's hypothesis. This question, however, concerns the investigating specialist much more than the general reader.

No more striking instance can be given of the development of chemical science during the past fifty years than the disappearance of speculations on the nature and the cause of "affinity," which is now pronounced of little or no use in explaining chemical phenomena. To the numerous class of persons for whom this work has been more especially written it must be pronounced invaluable.

A Dictionary of the Coal-Tar Colours. Compiled by George H. Hurst, F.C.S., Member of the Society of Chemical Industry. London: Heywood and Co., Ltd.

This is a work which was very much needed. The coal-tar colours are so many in number, and they have received from patentees and manufacturers such a number of synonyms,—often very inappropriate,—that both the student and the practical dyer have often been no little perplexed. It may be necessary to explain what we mean by inappropriate names.

As a striking instance we may point out Indian yellow. This name has long ago been used as a synonym for *purree*, but now it has been seized upon by a German firm and applied to the colour better known as "azo-yellow" or "azo-acid yellow." Harmaline, which properly pertains to a proximate principle extracted from *Peganon harmala*, has been applied to an impure magenta.

Other objectionable names are phloxine, fuchsine, roseine, cyclamine, and many others which might lead to the mistaken impression that they were vegetable proximate principles.

As instances of names which cannot occasion any such confusion may be mentioned Titan brown, orange, and pink, Stanley red, the Gambines, the azines, and many others. This confusion, however, is not in any way due to the author. His task has been not to reform but simply to explain the existing nomenclature.

We have not detected in the work anything which can be considered an error. A few artificial colours are omitted, but they are such as have been superseded or have never come into industrial use at all. Such are benzoyl blue (a mere mixture), isopurpuric acid, aveline, &c. Canarine, it might be objected, is not a coal-tar colour at all. But this frivolous complaint might have been at once excluded if the work had been entitled "Dictionary of the Artificial Colours." The introduction and the general remarks on dyeing and printing are ably and judiciously written.

It might save much trouble if the British Patent Office were authorised to reject specifications of the class which we have pronounced to be inappropriately named.

We consider that Mr. Hurst by compiling this work has conferred a very great benefit upon the tinctorial industries of this country, and we trust that it will find a place at every dye and print-works.

A Short Text-Book of Inorganic Chemistry. By Dr. Hermann Kolbe, late Professor of Chemistry in the University of Leipzig. Translated and Edited by T. S. Humpidge, Ph.D., B.Sc., late Professor of Chemistry in the University College of Wales, Aberystwyth. With a Coloured Table of Spectra and numerous Wood-Engravings. Third Edition, revised by H. Lloyd Snape, Ph.D., D.Sc., Professor of Chemistry in the University College of Wales. London: Longmans, Green, and Co. 8vo., pp. 616.

We have long regarded Kolbe's "Inorganic Chemistry" as one of the very best text-books which can be put in the hands of a student, and we are not surprised that even in this land of chemical manuals a third edition is already found needful. In Dr. Humpidge's preface,—which is here reproduced,—we notice, not without regret, the utterance that "in adapting the book for English students certain alterations and additions were necessary." It might have been well if these "alterations and additions" had either been given in the form of notes or had been marked out in the text by the use of distinct type. Readers who, like ourselves, have cherished the belief that science is the same in all countries, must naturally feel curious to know wherefore and in how far they have been mistaken? Certainly the final sentence of the preface throws some light on this point. The German original was written to meet the requirements of students who are working to *know*, and to add to the sum total of our chemical knowledge. But in the English version the "needs of students working for examinations have been steadily kept in view."

The appendix and the notes which have been supplied by the editor for the purpose of keeping the work on a level with the present state of knowledge are judicious and useful.

Two curious facts here mentioned (p. 134) should stimulate further research,—the failure of experimentalists to obtain hitherto a carbon fluoride and a fluorine oxide. We thoroughly approve of the recommendation that for the detection of arsenic in chemico-legal cases magnesium should be used in the Marsh process in the place of zinc.

CORRESPONDENCE.

LABORATORY STILLS.

To the Editor of the Chemical News.

Sir,—In reply to Mr. W. J. Cooper I may venture to assert that the law regarding stills was never meant to apply to those in use in private laboratories or chemical factories. I was recently engaged in a case (Regina *v.* Illingworth) in which it was successfully contended by the defendant's solicitor that the intention of the Act is to prevent the manufacture of liquors which are illicit, and surely distilled water is not one of them! In the case mentioned the Revenue people were attempting to impose a licence on a manufacturer who used a sulphate of ammonia still. The Bench of West Riding magistrates decided that "this still is not within the meaning of the Act." An appeal to a higher Court fell through on account of the death of the defendant.—I am, &c.,

Wm. Ackroyd.

Borough Laboratory, Halifax,
March 28, 1892.

LABORATORY STILLS.

To the Editor of the Chemical News.

Sir,—Your correspondent, W. J. Cooper, has legally incurred a fine through having a still on his premises without either having paid for a license or having received permission from the Board of Inland Revenue to use the same. He must address his request to the Commissioner of Inland Revenue, Somerset House, London, showing clearly that the still is used by him for chemical research.

The Board of Inland Revenue are very ready to allow stills free of excise license when it is proved beyond a doubt that they are wanted purely for scientific purposes, but *they must be asked permission* first. They have in the last few months also, to our certain knowledge, given permission to several directors of laboratories to obtain unmineralised methylated spirit.

We have had no case of the kind refused, and have forwarded several applications on behalf of the heads of laboratories to them. They are not so black as they are painted, but it must be made clear to them that stills are not wanted to manufacture articles for wholesale or retail sale, and that unmineralised methylated spirit is not required to sell, or by a party who also gets the mineralised article, as if this be the case they have to be stricter to protect their revenue.—We are, &c.,

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 11, March 14, 1892.

Researches on Samarium.—Lecoq de Boisbaudran.—The author has had placed at his disposal by Professor Clève about 3 grms. of the best samaria which he has ever possessed, and which he has fractionated with ammonia, but without obtaining the distinct separations hoped for.

On Certain very Definite Alloys of Sodium.—M. Joannis.—The author has obtained the compound, Pb 81·62, Na 18·38 per cent, contaminated, however, with a sodium amidide. On exposure to the air this compound heats strongly and in contact with water is decomposed, leaving soda and lead in the form of black flocks. The alloy of lead potassium, Pb_2K, is obtained by the action of an excess of potassammonium upon lead. Bismuth-sodium alloy, $BiNa_3$, is obtained in an analogous manner. It ignites spontaneously in the air, throwing up a splendid sheaf of sparks. It is decomposed by water with an escape of pure hydrogen. Antimony-sodium alloy, $SbNa_3$, is obtained in a similar manner. It ignites on exposure to air, and is decomposed by water with an escape of pure hydrogen.

The Assay of Antimony Ores.—Ad. Carnot.—This paper will be inserted in full.

The Vegetation of the Vine.—L. Ross and E. Thomas.—The saccharose formed during the ten or twelve first weeks of vegetation disappears in the leaves, the shoots, and even in the grapes, in the fourth month of vegetation. They then contain a mixture of sugars in which dextrose predominates. It is not always true to say that the acidity of fruits decreases as they approach maturity. The decrease of acidity in absolute value is observed at the moment when the levulose is decidedly increasing in the fruit. The polarimetric deviation passes to the left and increases progressively up to ripeness, when it is approximately equal to that of invert sugar.

Citric or Oxycarballylic Acid.—G. Massol.—In this thermo-chemical paper the author concludes that the formation-heat of potassium and sodium citrates in the

solid state is greater than that of the corresponding carballylates.

Some Reactions of the Isomeric Amido-Benzoic Acids.—Oechsner de Koninck.—Potassium, sodium, magnesium, and zinc, if heated in the absence of air with amido-benzoic acids, produce variable quantities of ammonia. If the same acids are heated with potassa, soda, baryta, strontia, magnesia, anhydrous or hydrated, zinc oxide, &c., we also observe the liberation of various proportions of ammonia. The various metals, oxides, and hydrates just mentioned do not develop the same colouring-matters with the three amido-benzoic acids.

Calculation of the Boiling-Temperatures of the Derivatives of the Paraffins by Terminal Substitution.—G. Hinrichs.—This paper requires the accompanying complicated diagram.

The Pyrogenic Carbides Formed in the Manufacture of Compressed Gases.—A. Brochet.—Among the numerous ethylenic carbides which may originate, the author has been able to identify six.

The Specific Gravity of Silks.—Leo Vignon.—In reply to M. de Chardonnet the writer maintains that the figures given by the latter are applicable not to silks in their original state but to specimens more or less "charged with metallic compounds."

Glycolysis in Blood.—Maurice Arthus.—Glycolysis in blood is a phenomenon of chemical fermentation. The ferment does not pre-exist in the blood, but is formed outside the organism at the expense of the white corpuscules, and seems to be in relation with the extravascular life of these elements. Glycolysis may be effected in the absence of elements actually living. It is effected exclusively outside the circulatory system like coagulation, with which it present important analogies.

Bulletin de la Société Chimique de Paris.
Series 4, Vol. vi., No. 70.

Report made by M. Jungfleisch on behalf of the Committee of Chemical Arts upon the Frigorific Appliances Installed at the Morgue.—The Morgue having become an annoyance and possibly a danger to a very densely populated locality, it has been resolved to employ refrigeration. It was required that the bodies on their arrival at the Morgue should be exposed to a temperature of $-15°$ to $-20°$. They were then to be placed in a hall in which the temperature should range from $-4°$ to $-1°$, and which should admit of ten bodies being preserved at a temperature of $-4°$. The system of refrigeration employed is that of F. Carré, the agent in which is liquid ammonia. The apparatus acts by physical and not by mechanical means, as on account of the situation everything calculated to occasion oscillation had to be avoided. The hall in hot weather requires an hourly supply of 13,000 "frigories."

On Lighting Gas.—Prof. Vivian B. Lewes.—From the *Journal of the Society of Arts.*

No. 71.

This issue contains no chemical papers.

MISCELLANEOUS.

The Chemical Laboratory of Wiesbaden.—In the winter term, 1891-1892, there were fifty-four students on the books. Of these thirty-nine were from Germany, three from Russia, three from North America, one from Luxemburgh, one from Switzerland, one from France, one from Holland, one from Belgium, one from Spain, one from Sweden, one from Batavia, and one from the Cape of Good Hope. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and architect J. Brahm. The assistants in the instruction laboratory were three in number, in the private laboratory twelve, and in the Versuchsstation three. The next summer term begins the 25th of April. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Mine Surveying," by Bennett H. Brough, Assoc.R.S.M.
—— Society of Chemical Industry, 8. "On Specific Gravities for Practical Purposes," by Dr. C. R. A. Wright, F.R.S. "On Artificial Musk," by Adolphe Baur, Ph.D. "Note on Rosin Oil," by F. H. Leeds, F.I.C., F.C.S.

TUESDAY, 5th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "The Red and White Races in Manitoba and the North-West," by the Rev. John McLean, D.D.

WEDNESDAY, 6th.—Society of Arts, 8. "The Future Trade Relations of Great Britain and the United States," by Robert McCormick.
—— Geological, 8.

THURSDAY, 7th.—Royal Institution, 3. "Epidemic Waves," by B. Arthur Whitelegge, M.D., B.Sc.
—— Institute of Electrical Engineers, 8.
—— Society of Arts, 4 30. "The Agricultural Needs of India," by Dr. J. Augustus Voelcker.
—— Chemical, 8. "Platinous Chloride and its Use as a Source of Chlorine," by W. A. Shenstone and C. R. Beck. "The Action of Silicon Tetrachloride on Substituted Phenylamines," by Prof. Emerson Reynolds.

FRIDAY, 8th.—Royal Institution, 9. "Electric Meters, Motors, and Money Matters," by Prof. W. E. Ayrton, F.R.S.
—— Astronomical, 8.
—— Physical, 5. "Note on a Law of Colour in its relation to Chemical Constitution," by William Akroyd. "On the Construction of a Colour Map," by Walter Baily, M.A. "A Mnemonic Table in connexion with Electrical Units," by William Gleed, M.A.

SATURDAY, 9th.—Royal Institution, 3. "Dramatic Music, from Shakspeare to Dryden," by Prof. J. F. Bridge, Mus. Doc.

ERRATA.—P. 147, col. 2, line 16, *for* "CrO_3" *read* "OrO_3. Line 42, *for* "CrO_3" *read* "Cr_2O_3."

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Experimental Physics	W. FRESENIUS, Ph.D.
Stöchiometry	
Organic Chemistry	E. HINTZ, Ph.D.
Chemical Technology	
Microscopy, with exercises in Microscopic work	Prof. E. BORGMANN, Ph.D.
Chemistry and Analysis of Foods ..	Prof. H. FRESENIUS, Ph.D. Prof. E. BORGMANN, Ph.D. W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene	Dr. med. G. FRANK.
Practical exercises in Bacteriology ..	
Technical Drawing, with exercises ..	J. BRAHM.

The next Session commences on the 25th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

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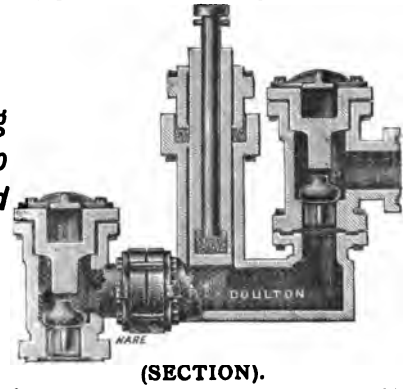

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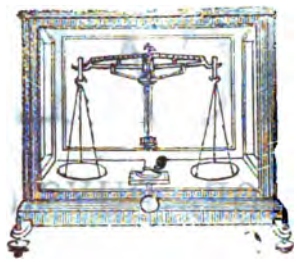

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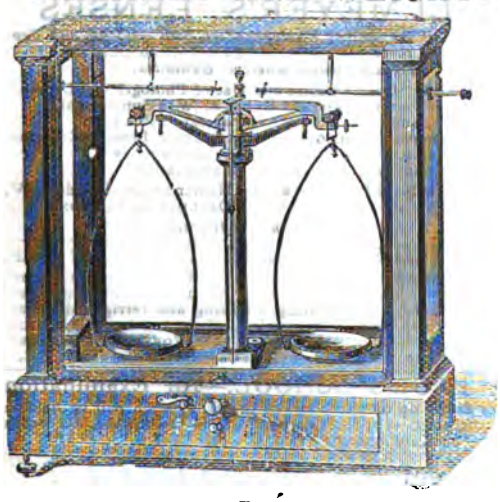

FIG. 32.

SHORT BEAM BALANCE, Fig. 32, No. 12a, to carry 2000 grains in each pan, sensible to 1-300th grain. Agate bearings, one rider apparatus. Nickel pans, 3 in. diameter.. £7 6 0
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THE CHEMICAL NEWS.

Vol. LXV., No. 1689.

RELATION OF VOLTAIC ELECTROMOTIVE FORCE TO MOLECULAR VELOCITY.

By G. GORE, F.R.S.

In a recent research published in the *Proc. Birm. Phil. Soc.*, vol. viii., p. 63, 1892, it is shown by means of an extensive series of sixty-four tables of measurements of *mean* volta-electromotive force, that the *dilution* of the liquid of a voltaic cell by means of water or alcohol, the *liquefaction* of either the positive or negative metal of the cell by means of mercury, the *dilution* of either of these amalgams by means of mercury, or the *dilution* of one solid metal by means of another in an alloy, is universally attended by an increase of *mean* electromotive force of the diluted and diluting substances, and consequently also of the *actual* electromotive force of the diluted one, provided that in all cases no chemical union or other chemical change occurs in the mixture. The manifest explanation of this extensive general result is, that by the act of solution or dilution, the molecules of the active substance are separated farther apart, and consequently acquire increased velocity of motion. In proportion, however, as chemical union occurs, the gain of electromotive force diminishes and is converted into a less, and the loss is larger in proportion as the chemical union is stronger. The method enables chemical compounds in alloys, amalgams, and electrolytes to be distinguished from mere mechanical mixtures.

THE ACTION OF ALKALINE MERCURIC CYANIDE ON MALTOSE, DEXTROSE, AND DEXTRIN.

By J. ARTHUR WILSON.

Commercial glucose or starch sugar, as is well known, consists of varying proportions of dextro-glucose, maltose, and dextrin, together with more or less unfermentable matters. It is also well known that the accurate determination, nay even the approximate determination, of each of these carbohydrates is very difficult indeed; but for most purposes this is not necessary, the determination of the specific rotatory power and reducing power being all that is necessary, giving, as it does, an insight into the composition of the sample. In Allen's "Commercial Organic Analysis" (vol. i., p. 303), it is stated that alkaline mercuric cyanide has been applied by H. W. Wiley to the analysis of commercial starch glucose. This reagent is said to destroy the optical activity of dextro-glucose and maltose, whilst leaving that of dextrin unchanged. Further on in the work above mentioned (p. 304), it is said that "On the other hand, it has not been proved that boiling with alkaline mercuric cyanide wholly destroys the optical activity of maltose and dextrose, whilst leaving that of dextrin unchanged."

I have long since felt the want of an accurate process for the above purpose in the control of a well known industrial process, so that it was with feelings of pleasure that I turned my attention to investigate the truth or otherwise of the above statement. My experiments do not pretend to be at all exhaustive, but I think they prove that the method is of very little use for the determination of the proportions of a mixture of dextrose, maltose, and dextrin.

Solutions were prepared of maltose, dextrose, and dextrin, containing 10 grms. per 100 c.c. of pure substance. The *purity* of these sugars was proved by determination of the cupric oxide reducing power and also of the specific rotatory power.

The method of proceeding was as follows:—The optical activity of the solution was first determined. 10 c.c. of the sugar solution (= 1 grm. dry sugar) was boiled two minutes with a slight excess of solution of alkaline mercuric cyanide, made by dissolving 12 grms. pure mercuric cyanide and an equal weight of pure caustic soda in 100 c.c. of water. The solution was then cooled, acidified by HCl, and diluted to 50 c.c. After clarification by pure animal charcoal the solution was polarised in a 200 m.m. tube.

The results were as follows:—

Maltose.

Solution 10 grms. per 100 c.c.
Polarisation 200 m.m., (A)d +26·0.
Polarisation after boiling with alkaline cyanide, 200 m.m. (A)d +1·8.
Polarisation on original concentration, +9·0.
Polarisation destroyed, +17·0.

No. 2.—Second experiment, but boiling four minutes, gave the same results.

Dextrose.

Solution 10 grms. per 100 c.c.
Polarisation 200 m.m., (A)d +10·85.
10 c.c. = 1 grm. boiled two minutes with slight excess of alkaline cyanide, cool, acidify, and dilute to 50 c.c.
Polarisation 200 m.m., (A)d +0·00.

Dextrin.

Solution 10 grms. per 100 c.c.
Polarisation 200 m.m., (A)d +37·2.
Polarisation after boiling two minutes with alkaline cyanide, (A)d 200 m.m. +6·7.
Polarisation on original concentration, (A)d + 33·5.

Loss, +3·7.

The results of the above experiments show that the method of Wiley is of very little use for the examination of commercial starch glucose. I should like to mention that the dextrin used in the above experiments was not quite pure, but not sufficiently impure to account for the loss given above. The fact that the optical activity of dextrose is completely destroyed in the above reaction might make the method of some use for mixtures of dextrose and other sugars.

Tottington, March 29, 1892.

ON THE COPPER AND SILVER COMPOUNDS OF ACETYLENE.

At the last meeting of the Chemical Section of the Franklin Institute, Dr. E. H. Keiser gave an account of an investigation upon the composition of the explosive copper and silver compounds of acetylene. The paper will be published at length subsequently. The results obtained are in brief as follows:—When pure acetylene is conducted into an ammoniacal solution of silver nitrate, the yellowish white precipitate which is formed has, when dried, the composition represented by the formula C_2Ag_2. It may in fact be regarded as acetylene in which both hydrogen atoms have been replaced by silver. The formula that has generally been adopted for this substance is $C_2H_2Ag_2O$. But such a compound contains only 83·71 per cent of silver, whereas in three specimens of the substance prepared by Dr. Keiser the quantity of

silver found was 89·32, 89·44, and 89·60 per cent. The formula C_2Ag_2 requires 89·9 per cent silver. That the compound contains no hydrogen was shown by exploding a weighed quantity of it in a glass tube which had been exhausted with an air-pump; no hydrogen was obtained.

A study of the compound formed by acetylene in ammoniacal cuprous chloride showed that it was similar in composition to the silver compound, although in this case it was much more difficult to obtain the substance perfectly free from water. Analyses showed that the composition of the substance after it had been dried in a vacuum over sulphuric acid agreed very closely with what would be required by the formula $C_2Cu_2.\frac{1}{2}H_2O$. The investigation will be continued.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg.

(Continued from p. 159).

III.—*Melting of Steel.*

IN starting a new branch of manufacture of special steel out of new materials, we prefer the use of coke crucible furnaces. The latter are cheap in construction, and the best thing is that while using them for experimental purposes they may be lighted or stopped any moment, with no inconvenience. That is not the case with the Siemens gas crucible furnace.

After many difficulties, we started the manufacture of tool steel for the market. The price was ten paper roubles per pood.

The gas furnace made on the average 4 to 4½ heats per twenty-four hours. The steel was ordinarily cast into 1½ and 2 pood ingots, 4 inches square; moulds being used. The ingots, after careful cleaning by chisels, were forged, The resulting bars, after inspection, were finished under a 1½ cwt. quick-motion steam hammer.

We made for the market three grades of tool steel: No. 12, for planing tools; No. 10, for drilling tools, chisels, and wood-working implements; No. 8, for cutting and stamping tools. These three grades contained in succession, on the average, 1·20, 1·00, and 0·85 per cent of carbon. The percentage of the other elements was as follows:—

	Per cent.
Manganese	0·18
Silicon	0·20
Sulphur	0·02
Phosphorus	0·03

In melting for tool steel, we used a mixture of puddled steel, old crucible steel, and Swedish cast-iron, or a mixture of Swedish iron and Swedish cast-iron. Each crucible charge (62 pounds) contained two-thirds of a pound of ferro-manganese. Very hard tools, specially ordered, were made out of steel prepared by melting a mixture of blister steel, Swedish cast-iron, and a small quantity of silicon spiegel (⅔ of a pound) containing 10 per cent of silicon and 14 per cent of manganese. This compound has a quieting effect on the blister steel, which melted alone and cast into moulds very often gives rising ingots.

We prepared pattern casting for many purposes, especially for some parts of the torpedo boats built at the Poutiloff Works. The crucible charges contained a mixture of puddled steel, basic steel, Swedish cast-iron, and about ⅔ of a pound of ferro-manganese. Each heat took about five and sometimes six hours. The additions to the steel before pouring it into the pattern moulds consisted of nearly 1·25 per cent of the above-mentioned silicon spiegel. When casting small articles, we used ferro-aluminium, but always in company with silicon pig-iron (for a charge of 62 pounds, 0·6 of a pound of the former and latter alloys).

We desire to say a few words concerning the preparation of ferro-aluminium. As already mentioned, we used American aluminium, coming from the Pittsburg Reduction Company (CHEM. NEWS, vol. lxv., p. 133). The best way to prepare the ferro-aluminium is as follows:—

Equal numbers of empty and charged crucibles were placed in the Siemens furnace. The charge consisted of 70 per cent of good grey pig-iron and 30 per cent of silicon pig-iron (10 per cent of silicon).

When the charges are melted, every time two crucibles are drawn out—one charged and one empty. Into the latter, 12 per cent of aluminium is added and the melted charge is quickly poured on to it; the mass is well stirred by means of an iron rod and re-poured again into the emptied crucible. Finally, the aluminium melts and the alloy is ready.

Having made many experiments, we advise not to use aluminium in the metallic state; it must be used in the alloy form.

Taking into consideration cheapness and good effect produced, we prefer the use of a reasonable quantity of silicon spiegel as addition in making steel for solid pattern castings, which are to contain for this purpose about 0·25 per cent of silicon.

ON THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILISERS CONTAINING COTTON-SEED MEAL.*

By F. B. DANCY, A.B.

(Concluded from p. 163).

IT is believed that the disparity in all these cases is probably not so great as it should be; that is to say, that the incineration method as here used probably does not give the full content of phosphoric acid for this reason. The inferiority of the solvent power of nitric acid for phosphates to that of hydrochloric acid is well recognised. I believe that this inferiority is greater when the phosphate has been ignited. To test this an acid phosphate was chosen, of which 2 grms. were dissolved in nitric acid and hydrochloric acid, and the total phosphoric acid found to be 14·56 per cent. Another 2 grms. were then ignited for about the same length of time that it requires to incinerate 2 grms. of a cotton-seed meal fertiliser to complete ash and then dissolved in nitric acid. The determinations were parallel, so that each received the same amount of heating with acid, which was protracted. In the case of the ignited phosphate, undissolved portions were plainly manifest to the eye, and the percentage found was only 13·62. The undissolved portions were filtered out and readily yielded to hydrochloric acid, giving fulsome precipitate of phosphoric acid. Next, another 2 grms. were ignited and dissolved in hydrochloric acid, when the full content of phosphoric acid was readily yielded. Hence it is concluded that had hydrochloric acid been used to dissolve the six incinerated fertilisers employed in the above experiments, higher percentages would in all probability have been found. Fusion would have furnished an absolutely certain means of arriving at the undoubted maximum content of phosphoric acid, but time was limited, and simple incineration was resorted to on account of expedition; and solution in nitric acid instead of hydrochloric acid was employed after incineration, because, as the results were to be compared, it was advisable to employ the same solvent power in each case.

In addition to the six experiments described above,

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

attention is called to the following:—Two samples of cotton-seed fertilisers were procured in which another chemist had made determinations of *total* phosphoric by the nitric acid method. His *totals* were 9·13 and 9·33. I found by incineration and solution in hydrochloric acid 9·85 and 10·13, a difference of 0·72 per cent and 0·80 per cent respectively. Taking his own determinations of *insoluble*, the *available* by his analysis was 0·72 per cent short in the first instance (7·40 per cent when it should have been 8·12 per cent), and 0·80 per cent short in the second instance (7·50 when it should have been 8·30 per cent). The disparity here is excessive, but the fault is not due to the chemist, but to the method. Being one of the alternate methods of the Association of Official Agricultural Chemists, he had no reason to doubt its adequacy.

Having looked at one side of the determination of *available* phosphoric acid in fertilisers containing cotton-seed meal, let us turn to the other, namely, the determination of *insoluble*. As almost the entire content of phosphoric acid in the meal has been shown to be available, it might be anticipated that there would not be likely to be much difference in the determination of *insoluble*, whether the citrate-extracted residue is first incinerated or dissolved directly in acid. Such was found by experimentation to be the fact. In fact, in every case but one (and this was the same fertiliser that was the exception to the *total* rule, namely, the old one brought from the previous season) a slightly higher *insoluble* was found by dissolving in acid directly than after incineration.

The details of the two methods of determining the *insoluble* were these: After filtering from the citrate and thoroughly washing, the filter and contents were in the first instance incinerated and the ash dissolved in nitric acid (designated in the table below as "incineration"), and in the second instance the filter and contents were introduced directly into flasks and completely dissolved with nitric acid and a little hydrochloric acid (the "acid solution" of the table below). The samples used were the same as those used in the total experiments, with the exception of 110, which was not used.

	Insoluble phosphoric acid.				
	56.	76.	77.	78.	57.
Incineration ..	0·84	1·80	0·86	0·87	1·59
Acid solution ..	1·00	1·91	1·28	1·05	1·42
Difference ..	0·16	0·11	0·42	0·18	—

Whether the excess of *insoluble* by direct acid solution was due to mechanical loss in the incineration by the other method (which in these instances is not at all apprehended, though it is believed that care is necessary to, with certainty, guard against such loss), or whether, as is much more likely, it was due to imperfect solution of the ignited phosphate by nitric acid (a danger already pointed out), is not positively shown. But it should be remarked that in the case of 77, which is the case of greatest disparity, the undissolved portions were manifest to the eye, and it is the writer's conviction that had hydrochloric acid been used instead of nitric, there would have been no material difference in the results of the two methods, either in these particular determinations or in any other determinations. It is regarded as certain, therefore, that there will be found no material difference in the *insoluble* by whichever way determined.* This being true, the *available* will vary directly and exactly as the *total*; and, therefore, by just so much as a *total* is short on account of the inadequacy of the nitric acid method when used on cotton-seed meal fertilisers, by just so much will the *available* be short.

Now a few words as to what method *is* adequate, and a very few experimental determinations on this point, and the subject will for the present be laid aside. It is a matter of regret to the writer that the time was not at his disposal for more extended experimentation on the subject, Nevertheless he is none the less convinced, on account of the limited number of experiments here presented, of the truth of the point urged.

In order to compare the *total* as made by several different methods, sample 110 was chosen. This sample was sent by a fertiliser company, who took a fair sample of a large lot of goods at their factory, thoroughly mixed the sample, and sent one-half to the writer and one-half to a chemist in another State. The *total* was determined first by fusing 2 grms. of the fertiliser with a mixture of equal parts of carbonate of soda and nitrate of potash, as giving with certainty the maximum content and furnishing a standard for comparison. It was then determined by incineration and solution in hydrochloric acid, by incineration and solution in nitric acid, by solution direct in hydrochloric acid with chlorate of potash, and lastly by solution direct in nitric acid and a little hydrochloric acid. Following are the results:—

	Per cent.
Fusion	10·14
Incineration and solution in HCl ..	10·09
,, ,, HNO_3 .	10·07
Solution direct in $HCl + KClO_3$ ..	10·11
,, ,, HNO_3 + little HCl	9·56

From the above it seems that in this case all the methods save the nitric acid methods were adequate, but it is not apprehended that this will hold good in all cases; for, while here incineration and solution in nitric acid sufficed, there is certainly the danger of imperfect solution already referred to; and while here also solution in hydrochloric acid with potassium chlorate sufficed, it has already been shown that this method failed to extract from the meal alone more than half its content of phosphoric acid.* Fusion is, of course, always adequate, but too time-consuming, if any other adequate method less so is at hand. It seems probable that incineration and solution in hydrochloric acid furnishes all that could be desired.†

It is in point to add that in this case the writer reported to the manufacturers a *total* of 10·11 per cent, this being an average of the first four determinations. The *insoluble* found by incineration and solution in hydrochloric acid was 1·47, making an *available* of 8·64. It is not known what method the chemist used to whom the other half of this sample was sent, but his *total* was 9·72, his *insoluble* 1·50, and his *available* therefore 8·22. Note that the two *insolubles* are practically the same, and that, therefore, his *available* is less than the writer's by practically the same amount that the writer's *total* is greater than his.

The following results, obtained on sample No. 3 (containing cotton-seed meal) of the samples sent out by Dr. Burney, the reporter on phosphoric acid for 1890, were submitted to that reporter, and are here appended as corroborative of the conclusions reached in the foregoing paper:—

	Per cent.
I. Total P_2O_5, by evaporation with $Mg(NO_3)_2$, ignition and solution in HNO_3	12·10
II. Total P_2O_5, by simple incineration and solution in HCl	12·08

* Corroborated by determination on phosphoric acid, reporter's sample No. 3, which showed:—

	Per cent.
Per cent insoluble P_2O_5 by ignition and solution in HCl ..	2·67
Per cent insoluble P_2O_5 by dissolving filter and all in HC_2 and a little HCl (without igniting)..	2·64

* It did not suffice in sample No. 3 sent out by the reporter on phosphoric acid.

† Corroborated by determinations in sample No. 3 sent out by the reporter on phosphoric acid, which showed:—

	Per cent
Total P_2O_5 by ignition with $Mg(NO_3)_2$ and solution in HNO_3	12·10
Total P_2O_5 by simple ignition and solution in HCl	12·08

	Per cent.
III. Total P_2O_5, by solution in $HCl+KClO_3$, two determinations (11·78 and 11·74) averaged .. :	11·76
IV. Total P_2O_5, by solution in HNO_3 + little HCl, two determinations (11·49 and 11·56) averaged .. :	11·53
I. Insoluble P_2O_5. After filtering from citrate solution and thoroughly washing, the filter and contents were ignited and dissolved in HCl	2·67
II. Insoluble P_2O_5. After filtering from citrate solution and thoroughly washing, the filter and contents were put direct into a flask and dissolved in HNO_3+little HCl	2·64

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Section B.—Chemistry and Mineralogy.

Address by the President,

WILLIAM M. HAMLET, F.I.C., F.C.S.,
Government Analyst, N.S.W.

When I became aware of the honour conferred upon me in being elected to the presidency of this Section, the question arose in my mind as to what the scope and character of the time-honoured Presidential Address ought to be. Should we bring before us the old platitudes and mystic half-truths embodied in the obsolete theories of the past, or, on the contrary, should we not try to obtain a clear presentment of recent advances in the science? and to recognise, in fact, the real benefits conferred upon the race by our increased knowledge: to recognise that the advance onward is always towards raising and bettering the lives of those around us, to finally become the heritage of those who follow us in the chain of life. Nor is it the only function of a President to convey to his hearers the *résumé* of the year's work; this may be better done by the numerous and increasingly bulky year books. Who amongst us does not remember the revered name of many a President of the older Association in Britain who presented the everyday facts of our science in such a clear and attractive manner that we thought no more of the toil and the unyielding patience required in our work, but only of the high aims and possibilities, of the ultimate unity and full relationship of all natural knowledge. This sense sublime—

> "Of something far more deeply interfused,
> Whose dwelling is the light of setting suns,
> And the round ocean and the living air,
> And the blue sky, and in the mind of man:
> A motion and a spirit that impels
> All thinking things, all objects of all thought,
> And rolls through all things"—

was in no small degree fostered by such annual addresses. How many of our past Presidents have there not been who seemed to act as the sign-post pointing to the Elysian fields of new researches,—who, by their help, counsel, and encouragement, inspired the earnest labourer in the pursuit of truth, and led him on to new discoveries?

The progress of Chemistry and Mineralogy in Australasia, upon which it is my privilege to address you to-day, is, from the nature of the circumstances, slow and beset with many hindrances. And this chiefly because the greater portion of our energies are devoted to the estimation of the monetary value of the natural and commercial products around us.

Here, in this later known part of our planet, we needs must spend a great deal of our time in work that can only advance science somewhat indirectly; so that it might be said that the record of the year with regard to original research work, were it given in its entirety, would read very much like Falstaff's hotel bill, showing but a halfpennyworth of research to an intolerable deal of drudgery. This, I admit, must necessarily be the case with most of us in a new country, who if not engaged in teaching and organisation are compelled to spend our time in assaying minerals, or else in the pursuit of the agricultural, sanitary, or criminal investigations incidental to our rapidly growing centres of population. Chemists in Australia occupy places in the rear-guard of the advancing army of science; and while it may not be our fortune to be at the outposts skirmishing on the frontier of the knowable, yet we have daily recurring duties that are none the less necessary for the well-being of society; thus at least, we may presume to say that we indirectly help forward the general advancement of science.

Still, some work has been done during the year in spite of these drawbacks: and this includes the discovery of the alkaloids brucine and strychnine in the fruits of *Strychnos psilosperma*, by Professor Rennie and Mr. Goyder, of Adelaide, who find 0·32 per cent of the mixed alkaloids in some specimens sent them by Baron von Müeller.

Additions to our knowledge of the Australian gums and barks have been made by Mr. J. H. Maiden, of Sydney; the first gum recorded from one of the Tiliaceæ, or Linden blooms—a metarabic gum obtained from *Eckinocarpus* (*Sloanea*) *Australis*—has been examined, also the gum of the grass tree, and the resins in certain species of *Pittosporum* and *Araucaria*, while he finds the kinos of great aid in the diagnosis of the different eucalypts.

Conspicuous amongst Mr. Maiden's researches is his work on Wattle-barks,* which are found to contain from 15 to 46 per cent of tannic acid, and have already proved to be valuable for tanning purposes, and their cultivation found easily remunerative to the agriculturist.

Then may be mentioned Mr. Kirkland's discovery of gallium and indium in some specimens of blende from Peelwood, N.S.W., the details of which will form the subject of an interesting paper by Mr. Kirkland. The minute structure of several of our more important rocks and minerals is being carefully and thoroughly investigated by the Rev. J. Milne Curran, F.G.S., a gentleman who has lately been awarded the £25 prize and the medal of the Royal Society of New South Wales.

Not only is the presence of the rarer metals of interest, but it is satisfactory to note that some observers are making efforts to find out the actual state of combination in which elements occur. An instance of this has lately been mentioned to me by Mr. Atherton through Dr. Storer, who finds gold in the state of sulphide at Deep Creek, Nambucca, N.S.W. Quantities of the raw ore were treated with sodium sulphide, and the gold obtained as Au_2S_3, there being only the merest trace left unacted on.

Much of this kind of work needs to be done in the Colony; and if such questions were investigated by men who understand what they are doing, it would go a long way towards facilitating the operations attempted in the smelting works, where carbonates, chlorides, oxides, and sulphides are often expected each to yield to the same kind of treatment.

Much has been said, and is still being said—though chiefly by speculators and mining share manipulators—about the vast mineral resources of Australia, and glowing accounts are set forth (in the prospectus be it observed) of reefs, leads, and auriferous deposits innumerable, where the precious metals are supposed to exist in most comfortable and payable quantities. But, when operations are well advanced, there comes the inevitable awakening, when plain facts clearly indicate that nature is not to be flirted with, notwithstanding the potency of a prospectus. Machinery rusting in idleness, useless furnaces, and other lumber remain as monuments of the unfortunate practice of erecting mining plant before the nature of the mine is

* "Wattles and Wattle-barks," by J. H. Maiden, F.L.S., F.C.S. Second Edition. Sydney: The Government Printer, 1891.

sufficiently understood. The dearly-bought lesson is this—that it is impossible for men who lack the necessary training in metallurgy to embark in adventures which, if attempted in other walks of life, would be considered madness. Yet the non-fulfilment of the expectations of those who invest in mining properties is ascribed to any cause but the right one.

The easy-going nugget-finding days are past, and have become a matter of history, while modern mining demands, more than ever, a larger share of skill, perseverance, and hard work. Smelting and reducing operations must necessarily become increasingly difficult as the richer ores become exhausted and new difficulties present themselves.

The problems of to-day are:—

1. Treatment of the so-called refractory ores.
2. Winning the precious metals from low-grade ores carrying but a few ounces to the ton.
3. The extraction of the metals from minerals holding some objectionable metal, or rather a metal that at present embarrasses the smelter—such, for instance, as the presence of zinc and sulphur in the Broken Hill ores.

To presume to deal with anything like a solution of these difficulties is quite beyond both my province and intention; but I would like to remind you of the sort of difficulty that blocks the way to success in many mines throughout Australia; and I, moreover, desire to point out some course of action that may probably be adopted in the near future (if I may make use of the expression), while social and labour difficulties stand like lions in the path whenever these problems are broached. However, come when it may, I foresee a time when other processes will supplant the expensive and crude methods hitherto attempted. Already there are companies and mine proprietors who perceive the want of processes better adapted to meet particular cases, and we hear a good deal about chlorination and wet methods for the separation of gold and silver.

The principle underlying all wet methods whatsoever is the chemical action of the electro-negative molecules, oxygen or chlorine, rightly and economically applied to suit the particular kind of ore to be treated.

Where sulphur is the *bête noir*, oxygen may be advantageously used if the metal be convertible into a soluble sulphate. Sulphur being absent, or easily removable by preliminary roasting, as in a great number of cases, then we may bring into operation the vigorous action of the little chlorine molecule—an instance of the phenomenon of that subject of solution which is profoundly interesting the minds of the chemists of the present day.

Now, as the source of the world's chlorine supply is the common salt we see on our dinner tables every day, this familar and salutary article must become an object of absorbing interest. Strange as it may appear to many, it is hardly too much to say that the phenomenon presented to us of a spoonful of salt dissolving in a tumbler of water is under close observation, and forms the subject of investigation of the best chemical philosophers of our age.

It may also seem a strange and far-fetched idea, yet the attention now bestowed on the physical and chemical properties of the molecule in solution must eventually contribute to the perfecting of new methods of separating metals from other elements with which they are associated in the ore. Leaving the practical side of the subject for a time, let us see what is being done in this interesting domain of molecular mechanics,—let us track the chlorine molecule into space.

He who surveys the ever-widening boundary of modern chemistry cannot fail to be impressed with the increasing amount of attention bestowed on physical and general chemistry. It would seem as though a reaction had set in: instead of the appalling host of carbon derivatives, which no man can number, endless as they seem in their protean permutations, we see a desire on all hands to know more of the varying phases of matter which were formerly passed by as trivial or commonplace; to picture the atom in space; to form clearer conceptions of the rushing together of atoms in the act of combination,—in a word to know something more definitely about chemical action. Thus am I led on to the subject of the molecule *per se* — the free ion — the whirling, eddying, ether-embedded molecule.

Our present position finds us in possession of the well-established—may I not say, the Impregnable—theory of an all-pervading ether describable as an elastic solid endowed with a great degree of rigidity. From the time of Young onwards this working hypothesis has commanded the assent of all thinking men, confirmed and strengthened as it is by the classic and firmly-founded work of Sir William Thomson, and others who have approached the subject from all sides.

Clearer perceptions also prevail with regard to the discontinuous or heterogeneous nature of matter, even of those solids which appear to our senses and to our most refined and delicate instruments as perfectly homogeneous; moreover, the kinetic theory, not only of gases, but of all states and conditions of matter, has received general recognition.

Yet another theory will, I am sure, commend itself to your earnest attention—one I have thought a good deal about for some years past, and which has been touched upon by Mendeleeff eighteen months ago when lecturing at the Royal Institution in England.

The idea may be considered a wild speculation by some; but I am bound to believe, judging by analogy with the magnificent conceptions presented to us by modern astronomy, and by the observed behaviour of matter as shown lately by the work and discoveries of Crookes, Thomsen, Ostwald, Arrhenius, Van 't Hoff, and many others, that, just as the systems of worlds, suns, stars, and planets roll in limitless space, so rolls the atom; but at enormously increased velocities in symmetrical order like double stars, or in systems comparable to suns and their accompanying satellites—the complete self-existent undissociated molecule being comparable to a given solar system coursing through space.

The work of Maxwell, Faraday, Helmholtz, Lodge, Fitzgerald, Hertz, and Sir William Thomson, men, who, like Huxley's ideal possessor of a liberal education, can "spin the gossamers as well as forge the anchors of the mind," all contribute towards clearing up the mystery surrounding the thing daily handled and observed by the chemist—the familiar thing we call "matter."

Putting aside for the moment the idea as to whether the atoms are or are not portions of the ether differentiated off from the rest by reason of their vortex motion, we have in the omnipresent ether, at any rate, the space, the playground, for the atom, whose unseen but energetic movements we have learned to speak of as heat and chemical action.

Having, then, granted a place in the universe for the ubiquitous atom, the chemist must endeavour, however dimly it may be, to picture to his mind its relative position, its own proper motion, its translatory motion, and, above all, its influence upon the ether when rocked by the waves set up by vibrating masses of atoms at a distance. When this is known we shall be able perhaps to account for the specific differences presented to us by matter.

In its simplest aspect we may think of the substance of the universe, at least of that which appeals to our senses, as consisting of what we arbitrarily call matter, and of its smallest portion as the invisible atom—an idea held by ancient philosophers some three centuries before Christ; the smallest quantity assumed to exist freely in space under known conditions being the molecule. From what we have seen and from all we know of infinitely minute particles of matter, can we think or conceive that these molecules are huddled together like a chaotic heap

of bricks? Assuredly not,—at least not in a definite compound; and the truth is borne in upon us at the thought of the microscopic yet symmetrical crystal. Looking about for a familiar and universally known substance, we have in water an instance of a symmetrical molecular system, whether under the form of solid ice, liquid water, or gaseous steam, made up of three atoms.

It will greatly assist us in our contemplation of the molecule if for the nonce we magnify these atoms several million times beyond their actual size. We should probably see a small sphere rotating about their own axis, and at a given distance two larger spheres also rotating about their own axes, but travelling in a definite orbit around the smaller sphere, the three together forming a system revolving in one plane with its own individual precision, the whole system capable of moving at a great velocity in any possible direction.

Calling these individual planets in the molecule by their received names, we see oxygen as a central sun with two large primary planets both called hydrogen, situate at equal angular distances from each other, but with nothing known at present to distinguish either of the hydrogen planets from each other.

Suppose, now, their orbital velocity be caused to diminish by friction and to finally cease, we should have each hydrogen planet distant 180° from one another. Placing three such systems with no orbital motion over each other so that the hydrogen satellites shall be equidistant, a straight line passing through and intersecting each of the centres of the oxygen spheres will form a hexagon.

Now, it is a fact that water in crystallising to snow and ice assumes the form of the hexagon. May not this cessation of the orbital motion determine the act of crystallisation, and, on the other hand, the widening and opening out of the orbit determine the expansion, while the friction of hydrogen against hydrogen satellite determines the heat caused by compression?

In trying to realise these things I have asked you to magnify the dimensions of the atom in the structure of matter; this has already been done, as you well know, by Sir William Thomson; but, as a better estimate of the size of the atom will be gained, his calculation will, I think, bear repetition. "Imagine," he says, "a globe of water or glass, as large as a football (or, say a globe of 16 c.m. diameter), to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion. The magnified structure would be more coarse-grained than a heap of small shot, but probably less coarse-grained than a heap of footballs."

A glassful of pure water, then, consists of an enormous and unthinkable number of molecules, each consisting of a complete system of atoms arranged by law in a definite and determinate order, like the orbs we see

"In the sacred glory of the azure night."

It follows that in this mass of water there must be intramolecular spaces, and that the molecules are everywhere throughout the liquid jostling, colliding, and sliding over one another. It also follows that, if we can communicate motion from without, the mere gliding of molecule over molecule will give way to sharp collision, impact succeeding impact, until the crowd of molecules is in a state of great internal commotion. Such an effect is brought about by the mere application of heat, and the energy of this motion is capable of being accurately measured.

This internal bombardment of molecules may proceed further, until cohesion and surface tension is overcome and the gaseous state is arrived at.

Regarding matter as being thus constituted, what should happen when we throw a few grains of salt into water? Clearly, it must be that as soon as the molecules of sodium chloride come within range of the water molecules friction and collisions ensue, the nearest salt molecules being driven into intra-molecular space. The amount of heat necessary to undo the crystalline structure—in other words, the motion acquired by the sodium chloride on coming into solution is abstracted from the water molecules; that is to say, work is done by the water molecules, hence a reduction of temperature in the liquid. Had we substituted potassium iodide with its greater molecular weight instead of the sodium chloride, the reduction of temperature would be greater. The solution of a salt in water may be regarded as the removal of molecule after molecule in the crystalline architecture, the whole mass finally reaching one uniform state of motion—*i.e.*, equilibrium of temperature and action. The molecules thus dislodged from their recent crystalline structure are free to spin through the liquid as double stars, having a diminished degree of attraction for each other owing to their approximately similar atomic weight. Thus it comes to pass that we have a stage of incipient dissociation, a large proportion of the atoms being liberated in the free state or dissociated into their ions,—a conclusion arrived at by Arrhenius in 1887, and quite independently by Planck in the same year.

The apparent decomposition of a salt solution, *i.e.*, an electrolyte into free ions, is considered by some to be a process of direction and not one of real decomposition; but I think myself that it is one of oscillation between mere direction on the passage of the current on the one hand and dissociation on the other.

In the present controversy between association and dissociation there is reason to believe the advocates of both systems to be right so far as the facts are concerned, the phenomena presented by the hydration of sulphuric acid not being on all fours with the facts brought to light in cases of salt solution. However, the day will soon dawn when the whole subject relating to chemical energy will be fully elucidated, and means found for its precise measurement. It is now a veritable mine of intellectual activity, and it is no wonder that new facts are constantly being recorded.

We may expect that, with such an array of facts such as are now given to the world by Ostwald, Van 't Hoff, Gladstone, Pickering, Arrhenius, Armstrong, and others—facts that slip easily into their proper places in the great fabric of Physical Science—that some master mind must sooner or later arise who shall so co-ordinate, interpret, and arrange them as to deduce therefrom the laws of chemical energy and affinity. Mendeleeff, in recognising this, bids us anticipate such a grand realisation. He says,* "the invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for astronomy and mechanics in the days of Newton." It is well to remember that Newton devoted much time to chemical experiments, and while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics.

As the avowed object of most of the addresses that are inflicted upon us should be "to point a moral: to adorn a tale," we ask ourselves, Is there no interest in this question of salt-solution for us here in Australia? I venture to believe there is. And thus we come back to the question of the action of solvents generally, and the practical application of them in what are called wet processes in mining and metallurgy.

The extraction of metals from their ores has been effected from time immemorial by the well-known methods

* "An Attempt to Apply to Chemistry one of the Principles of Newton's Natural Philosophy": a Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

of smelting, the object generally aimed at being the separation of the metal in the molten state by the addition to the ore of some mineral or earthy substance to cause the mixture to fuse, flow, or flux while subjected to the great heat of a furnace, the metal separating out by itself in a more or less pure condition.

The cost of such a scheme of well-planned operations as these will, of course, vary with the degree of richness of the ores, the cost increasing with the poverty of the ore treated, a limit soon being reached which depends on local and other conditions, and the poor ores can only be regarded as so much useless rubbish that will not pay for smelting. In such cases a wet process for extracting the metals might be advantageously employed, and we may dissolve the precious metals in a watery solution and collect them by suitable means. To the miner who is unfamiliar with such a process it sounds an impossible and an uncanny way of doing things. However, several wet methods commend themselves to the metallurgist in cases where the ores are too poor to be worked economically by any other means.

Speaking generally, the end in view is to obtain the metals in a soluble form, either as chloride, sulphate, or cyanide, and then to remove them from the liquid by precipitation. In this way we can separate out gold, copper, zinc, silver, and lead.

In the case of chlorination the sources of the active chlorine are:—

1. The decomposition of bleaching-powder either by acids or acid sodium sulphate.
2. The direct use of the chlorine liberated by electrolysis.
3. Roasting the ore with salt.

The first of these methods is open to serious objection owing to the wasteful loss of chlorine, and the difficulty of transporting oil of vitriol over rough country. Both of the other methods have much to recommend them in a country like Australia.

Amongst the simplest processes suitable for Australian ores—one adapted for the extraction of silver from ores not rich enough to pay for smelting, or from ores that do not easily yield to ordinary treatment—is the Joachimsthal process suggested by the late Dr. Percy and Von Patera, also known as Kif's method.

Many modifications and improvements have been made on the original process, and the names of Henderson, Claudet, and others are associated with it, the modifications being made to suit the great variety of ores treated.

The ore, broken small, dried if necessary, and crushed fine under the stampers, is mixed, with or without preliminary roasting, according to the nature of the ore, with 12—15 per cent of common salt, and roasted six to ten hours. The active chlorine molecule seizes the copper, lead, gold, and silver molecules to form the chlorides of these metals. On now soaking out the cooled product in water—the operation termed leaching—a portion of the now soluble metals are removed, being dissolved in the salt water. Allowing the earthy impurities to separate, this liquid is drawn off and set aside for after treatment. The roasted ore is further lixiviated by means of a cold solution of 1—2 per cent sodium thiosulphate, and added to the first liquor. From this the lead is removed as "white lead" by soda ash, yielding at once an article of commercial value, and the copper and silver are both separated out by precipitation with sodium or calcium sulphide; the product, containing 25 per cent of silver, is dried and roasted, being then available as a marketable commodity. This process has been successfully carried out at Rivertree, N.S.W., by Mr. Hall, of Brisbane, who finds that 85 per cent of the silver present in low grade ores may be obtained in this way.

Another process lately brought into use in Queensland and in Victoria is the "Pollok Chlorination Process," more especially adapted for gold ores. Chlorine under great pressure is employed to dissolve the metal, the gold being separated by an iron salt. The details of this process is given by the late C. S. Wilkinson, who inspected its working while in Glasgow about a year ago (Report, Mines Department for 1899, p. 213. Sydney: Government Printer, 1891). Mr. Wilkinson also described the Macarthur-Forrest cyanide process, in which a weak solution of potassium cyanide is used to dissolve out the precious metal, which is then removed by metallic zinc. The process is being worked at Ravenswood, in Queensland.

The chief considerations that have to be taken into account in any of these methods of working must necessarily include the question of easy transport across country of the materials to be used, and the presence of an adequate water supply. The future of silver reduction in Australia must surely be an interesting one to all chemists and metallurgists; and when the labour question shall have been righteously adjusted between man and man, and the spread of technical education produces the skilled workman, there will be no reason why minerals carrying what are now considered ridiculously small quantities of gold and silver should not be economically worked.

A promising step in the right direction is the idea of producing chlorine on the spot from common salt by means of the current of electricity from an ordinary dynamo. The production of chlorine by electrolysis is already a *fait accompli*, and bids fair to prove successful as a commercial undertaking. A process has been patented by Messrs. Richardson and Holland, and recommends itself on the ground of its portability, the materials requisite for working the same being easily transported over great distances. The principle is based on the fact that common salt is decomposed and resolved into its ions, as we have seen, the chlorine being set free next the anode and sodium at the cathode. The chlorine is collected from the surface, while caustic soda remains in the liquor. The chlorine may, however, be allowed to reunite with the sodium, as hypochloride, if desired. A drawback to its use at first was the resistance caused by the insertion of porous partitions used to separate the ions. This greatly militated against its commercial application, as did the polarisation caused by the evolution of hydrogen from the decomposition of the water present. To overcome these difficulties, the porous partition of the decomposing tank is reduced in size, and copper oxide is introduced to enable the hydrogen to combine with its oxygen, thus leaving behind metallic copper, which is re-oxidised by heating in a current of air and used over and over again. The process may obviously be used in the manufacture of caustic soda and sodium hypochlorite as well as chlorine, according to requirement.

(To be continued.)

Synthetic Formation of Acetylene at the Expense of Bromoform.—P. Cazeneuve.—Bromoform, in contact either with silver-powder or with moist zinc-copper, constitutes an abundant source of acetylene.—*Bull. de la Soc. Chim. de Paris.*

Detection of Isocholesterine.—E. Schulze (*Zeit. fur Phys. Chemie*).—The author utilises the colour-reactions produced with acetic anhydride and sulphuric acid. If the isocholesterine is dissolved in acetic anhydride with the aid of heat, allowed to cool, and a drop of concentrated sulphuric acid is added, the solution takes first a yellow colour, which passes into an orange. The liquid displays also a green fluorescence. If isocholesterine is dissolved in chloroform and acetic anhydride, and sulphuric acid are added, the same phenomena occur. This reaction is very sensitive, and serves for the detection of 1 m.grm. isocholesterine. Cholesterine reacts also with the same reagents, but the colours obtained are quite different from those of isocholesterine.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 25, 1892.

Professor S. P. Thompson, Vice-President, in the Chair.

Miss L. E. Walter was elected a member of the Society.

"*A Note on the Electromotive Forces of Gold and Platinum Cells*" was read by Prof. E. F. Herroun.

Modern text-books put gold before platinum in Volta's electropositive series, and thus one is led to expect a greater evolution of heat when gold combines with, say, chlorine than when platinum does so. This, however, is not the case: for Julius Thomsen gives for the heat of formation of platinic chloride a value considerably greater than that for auric chloride. Gold should therefore be electronegative to platinum. The few experimenters who have tested such cells arrived at different conclusions; hence the author took up the subject, and examined experimentally the E.M.F.'s of zinc-platinum and zinc-gold cells, the metals being immersed in solutions of their chlorides of equal molecular strength. Instead of platinic chloride, a solution of sodio-platinic chloride was employed. From Thomsen's thermo-chemical data, the E.M.F. of such a zinc-platinum cell should be 1·548 volts; whilst experiment gave values between 1·70 and 1·473, according to the previous history of the cell. The average E.M.F. was about 1·525. Allowing the cell to send a current reduced the E.M.F. considerably, but it partly recovered on standing. Renewing the sodio-platinic chloride reproduced the high initial E.M.F. of 1·7 volts. This high value and the uncertainty of the E.M.F. after sending a current the author believed due to dissolved oxygen. Zinc-gold cells, the metals being immersed in solutions of their chlorides, gave more constant results, the maximum being 1·855 and the minimum 1·834 volts; whereas from thermo-chemical data the E.M.F. should be 2·044. On replacing a gold plate by a platinum one, the E.M.F. fell to 1·782.

Other experiments showed that gold is slightly electropositive to platinum in water or dilute HCl, but in aqua regia the positions are reversed.

Prof. Ayrton said the experimental E.M.F.'s were fairly close to the theoretical values, and thought the differences might arise from occlusion of gases, which, although not taken into account in the thermo-chemical experiments, might have considerable effect on the electrical values. Platinum especially had remarkable occluding properties.

Mr. Enright pointed out that if any gases were disengaged by the reactions in the cells, their thermal values must be allowed for.

The Chairman (Dr. Thompson) believed that some discrepancy between the calculated and observed values of the E.M.F.'s might be due to the calculations only being carried to the first degree of approximation. The complete expression contained, amongst others, a term depending on the temperature coefficient of the cell. On the subject of variation of the sign of E.M.F. with the strength of solutions, he said he had observed similar effects with cyanide solutions.

Dr. Herroun, in reply, said care was taken to expel as much of the occluded gas as possible before using the plates, and no gases were formed in the reactions. To Dr. Thompson he pointed out that Clarke's cell had an E.M.F. greater than that calculated from thermo-chemical data; hence the temperature coefficient ought to be positive, but, as a matter of fact, it is negative. The discrepancy between the calculated E.M.F. and the observed he believed due to inaccurate determinations of the thermo-chemical constants of mercury salts.

A "*New Instrument for Showing the Effects of Persistence of Vision*" was exhibited and described by Mr. E. Stuart Bruce, M.A. The instrument, which the author calls an "aërial graphoscope," consists of a narrow wooden lath mounted on a whirling machine so as to be rotated rapidly in its own plane. The lath is tinted grey in the centre, and shades off to white at the ends. When rotated, it presents the appearance of a nearly uniform screen or disc, owing to persistence of impression. Ordinary lantern slides were projected on this aërial screen with remarkable effect, for the pictures appeared suspended in mid-air. The author explained that the object of darkening the lath near the middle was to give a more uniform illumination to the picture or disc. On covering up the centre portion of the lath with white paper, the middle of a picture projected on it was much more strongly illuminated than the edges.

Mr. Blakesley pointed out that the effect produced by darkening the centre of the lath might be attained by painting white sectors on a black lath.

A Paper on "*Some Electrical Instruments*" was read by Mr. R. W. Paul, and the apparatus exhibited. He first described a new form of standard ohm, the distinguishing feature of which is that the wire is wound in one flat spiral, and contained between two thin brass plates. The whole of the wire is thus practically at the same level in the water-bath, and therefore will be more likely to be at uniform temperature throughout than coils having considerable vertical depth. A thermometer passing down the central tube has its bulb on the same level as the wire, and another thermometer placed in the water-bath at the same level serves to check the uniformity of temperature. In order that the width of the coil may not prevent convection currents in the bath, the screws which fix the two brass plates together have large holes through them. Dr. Fleming's suggestion of forming the upper ebonite insulator into an oil cup has also been carried out.

A new form of Wheatstone bridge was next shown possessing all the advantages of the dial pattern, combined with great facilities for cleaning. There are four resistances in each proportional arm, and the adjustable arm has four sets of coils, units, tens, hundreds, and thousands, each set consisting of ten equal coils. The ends of each coil are connected to brass sockets fixed about an inch apart on the ebonite top. Successive coils are put in circuit by placing a plug attached to a flexible cord in the required socket.

Special contact bars are provided, whereby two or more coils of any set of ten may be put in parallel arc so as to get accurate resistances of large carrying capacity. These bars are also useful for obtaining high ratios between two resistances, a point of considerable importance in the testing of large resistances. Amongst the advantages claimed are—better insulation, avoidance of surface leakage by providing ample facilities for cleaning, small block error, which is constant and easily measured, and no loose plugs required. Each set of ten coils may be used as separate circuits. By means of two travelling terminals the box may also be used as a potentiometer reading to 1 part in 10,000.

A reflecting galvanometer with several improvements was then exhibited and described. The coil is supported on an ebonite pillar fixed to a tripod, below the centre of which controlling magnets on the Siemens principle are pivoted. The pillar gives good insulation from earth, and the adjustment of the control can be made without setting the needle in vibration. The two halves of the coil are wound according to Sir W. Thomson's law, and fixed in ebonite boxes turned to fit them. They are thus kept permanently in shape. The ebonite boxes are interchangeable, so that either high or low resistance coils can be used in the same stand. The coils have separate terminals, and can therefore be used in series or parallel, or differentially. The mirror is placed in a metal box

below the coil. When intended for an astatic instrument magnets are put behind the mirror, and the metal box serves to damp the vibrations. For ballistic work the mirror has no magnets on it, and the damping may be regulated by sliding in or out a plug which carries the window of the mirror box.

Mr. SWINBURNE inquired whether the plan of using two vertical magnets to form an astatic system had been tried, and with what result. He also asked if dial bridges made with switches instead of plugs would not be advantageous.

Dr. SUMPNER said vertical needles had been used at the Central Institution and found satisfactory.

Mr. A. P. TROTTER wished to know whether there was any very great advantage in designing galvanometers with a minimum amount of wire. A galvanometer was often required for many different purposes, and it did not follow that one with a minimum amount of wire was the best all-round instrument.

Mr. C. W. S. CRAWLEY made inquiries as to the magnitude of the block error in the form of Wheatstone bridge shown, for he thought the flexible cords would make it considerable. In reply to Mr. Swinburne he said he had found the variations in switch bridges greater than in plugs.

Prof. S. P. THOMPSON thought it was not generally known that the best shape of galvanometer coil depended on whether the instrument was to be used as an ammeter or voltmeter. The shape determined by Sir W. Thomson was a voltmeter coil; that for an ammeter was much shorter axially.

Mr. PAUL, in reply, said he used one or other shape of coil according to the use for which the galvanometer was intended. The block error in the Wheatstone bridge was very small and quite negligible for most purposes. When very great accuracy was required the error, being constant, was easily measured and allowed for.

NOTICES OF BOOKS.

Lessons in Elementary Chemistry, Inorganic and Organic. By Sir HENRY E. ROSCOE, LL.D., F.R.S., late Professor of Chemistry in the Victoria University, Owen's College, Manchester. London: Macmillan and Co., 1892. Small 8vo., pp. 503.

THIS favourite manual has now reached its sixth edition, besides having been many times reprinted with slight corrections. The author in his introduction considers the decomposition of some of the supposed elements into simpler ingredients as possible, or even likely.

The lessons on the periodic law, on spectrum-analysis, and on solar and stellar chemistry, are exceedingly valuable; quite equal, in fact, to what we often find in larger and more pretentious books.

The distinction between an organic substance and an organism is here clearly explained, and may save many students from dreaming of the synthesis of grain, fruits, &c.

On p. 339 we find an error doubtless clerical or typographic in its origin. It is there stated that "aluminium and *ferric* acetates are used in large quantities by dyers and tissue printers under the commercial names of red and black liquor." Iron liquor is not a *ferric* but a *ferrous* acetate.

At the end of the book there follow a number of questions and exercises which the student is advised to answer and to work out. But they are not said to have been "set" by any Board or Department, and throughout the book we can find no reference to any examination. This work must take rank among the few elementary treatises on chemistry which have a definite and legitimate *raison d'être*.

Soils and Manures. By J. M. H. MUNRO, D.Sc., F.I.C., F.C.S., &c. With chapters on Drainage and Land Improvement by JOHN WRIGHTSON, M.R.A.C., F.C.S. London, Paris, and Melbourne: Cassell and Co. Ltd., 1892. Small 8vo., pp. 275.

THIS work is one of the agricultural text-books published by Cassell and Co. under the general title "The Downton Series." Although one of the authors of this little book announces himself as "Examiner in Agriculture under the Science and Art Department," we find here no trace of the examinational taint. There are no lists of questions which have been asked anywhere on any occasion, and of course no sets of replies. The authors write not with reference to any possible examination, but with the wholesome and honest purpose of enabling their readers to *know*, and this purpose is very well effected. It is pleasant to see in what clear and simple language the nature of soils and the properties of their ingredients are explained, in a manner which certainly pre-supposes no chemical training on the part of the reader.

Humus, or vegetable mould, after having been first regarded as the sheet-anchor of the farmer and gardener, and then decried as next to useless, finds here a fair appreciation intermediate between these extreme views. The reader finds here that humus contains mineral food, is a store of nitrogen, keeps soils open, supplies carbonic acid, retains water, and absorbs manures.

Certain pieces of traditional wisdom current among our farmers, and too often simply ridiculed, are shown here to have in them a portion of truth. Thus, the proverb,—as we might almost call it,—that lime "enriches the father but impoverishes the son," is a one-sided expression of the great truth that no soil ought to be continuously manured with one substance only.

As real plant-foods the author enumerates nitrogen, phosphorus, potash, lime, sulphur, magnesia, chlorine, with a little soluble silica and a trace of iron oxide.

It is here decidedly admitted that leguminous plants procure nitrogen—though not necessarily all their nitrogen—from the air. The directions given for experiments, whether in the field or in pots, will prove very useful. The condemnation of nitrate of soda, and indeed of all chemical manures, as exhausting the soil, is shown to be founded on a myth. Agriculturists, both in France and Germany, are now considering that the keeping of stock on purpose to supply manure may be dispensed with. This, indeed, seems to have been thoroughly proved by Ville.

The remarks on sewage manure, especially when applied by irrigation, are very sensible. The writer says: "Large crops of rye-grass, mangolds, rhubarb, onions, cabbages, celery, osiers, and other produce can be, and are, grown on these farms, but not, as a rule, profitably. No one would complain much of this if the sewage ceased to be a nuisance, which is not always the case. There it is, Sunday and weekday, winter as well as summer, when the ground is bare as well as when growing a crop. Even if frost-bound for weeks there is the liquid to be disposed of somehow, the manager or farmer being in the position of having a very weak manure (valued at from a penny to twopence per ton), forced on him all the year round, instead of only the few months when he really wants it, and in quantities generally far greater than the land at his disposal requires."

Such outspoken truthfulness will in certain quarters not be heard without horror. Dr. Munro will next be "speaking holy words," if not to the Lord Lysimachus to some Royal Commissioner!

Almost the only shortcoming which we meet in this work is in the section relating to the value of manures. It must be admitted that manures have two distinct values, a commercial and an agricultural. Either of these may fluctuate independently of the other. The market value is a mere question of supply and demand; the agricultural value turns upon alterations in quality. A good

nstance of this is found in Peruvian guano. Since it was first brought into use the available supplies have been much reduced, some of the best deposits having been quite exhausted. Hence its commercial value has been well maintained. At the same time its percentage of nitrogenous matter has fallen off, whilst that of sand and moisture has increased. Hence its agricultural value has been reduced. The farmer can be recommended to buy a manure only if its agricultural value is decidedly higher than its market price. This work may be warmly recommended.

The Climatologist. A Monthly Journal of Medicine devoted to the Relation of Climate, Mineral Springs, Diet, Preventive Medicine, Race, Occupation, Life-Insurance, and Sanitary Science to Disease. Vol. II. No. 1.

We do not see that in this journal there is anything which falls legitimately within the purview of the CHEMICAL NEWS.

CORRESPONDENCE.

PROPOSED STANDARD METHODS OF WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—The importance of having standard methods of water analysis (especially technical water analysis), agreed to by chemists, at least in the United Kingdom, seems to me never to have been so necessary as at the present time. Now that authorities are being forced to do something to purify their sewage and works, their waste liquors from manufacturing processes, difficulties will arise, no doubt, as to the methods to be used of deciding the purity, or otherwise, of the water in question. Methods of determining the most common impurities are by no means what they might be, and the use of inaccurate processes may give rise to unpleasantness between parties.

The subject is a large one, and a deal of work would have to be done before any scheme could be adopted; nevertheless, it seems to me that this ought not to prevent an attempt being made. I trust, therefore, that chemists will expound their views in the columns of the CHEMICAL NEWS, and it is perhaps, further, not too much to expect that something may be done towards the realisation of this desirable end.—I am, &c.,

J. ARTHUR WILSON.

Tottington, March 30, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 12, March 21, 1892.

Study of the Properties of Amorphous Boron.—Henri Moissan.—This memoir will be inserted in full.

Preparation of Boron Iodide.—Henri Moissan.—A question of priority as between the author and M. Besson.

Origin of the Colouring-Matters of the Vine; on the Ampelochroic Acids, and on the Autumnal Colouration of Plants.—Arm. Gautier.—This paper will be inserted in full.

Determination of Chemical Equilibria in Dissolved Systems.—Georges Charpy.—This paper cannot be intelligibly reproduced without the accompanying diagram.

Combinations of Cuprous Iodide with Ammonium Hyposulphite.—E. Brun.—Three compounds may be obtained: $Cu_2I_2,2NH_4I,8[S_2O_3(NH_4)_2]$,

$$7[S_2O_3(NH_4)_2],(S_2O_3Cu_2),4Cu_2I_2,4H_2O, \text{ and}$$

$$S_2O_3(NH_4)_2,Cu_2I_2,H_2O.$$

The first of these bodies is soluble in water, but the two others are insoluble. All are gradually decomposed by heat. The potassium and sodium hyposulphites give analogous compounds, and other iodides, *e.g.*, those of silver and lead, produce similar substances which the author proposes to study.

The Speed of Decomposition of the Diazo-Compounds.—J. Hausser and P. Th. Mueller.—A mathematical paper not susceptible of useful abstraction.

On Certain Bases, Homologues of Quinine.—E. Grimaux and A. Arnaud.—The authors have obtained and studied the propylic, isoproylic, and amylic derivatives of cupreine.

The Essential Oil of Licari kanali.—Ph. Barbier.—The author has experimented upon licareol, $C_{10}H_{18}O$,—a colourless liquid extracted from the oil of licari. Licareol is of an alcoholic nature, and must rank among the secondary alcohols.

Combination of the Fatty Acids with the Ethylenic Carbides.—MM. Béhal and Desprez.—The authors have succeeded in fixing the fatty acids upon the ethylenic carbides, obtaining caprylene and heptylene acetates and the diacetine and propylglycol.

Natural Synthesis of the Vegetable Hydrocarbons.—M. Maquenne.—Heptine must take rank among the inferior homologues of turpentine, $C_{10}H_{16}$, or even menthene, $C_{10}H_{18}$, which is formed in the action of phosphoric anhydride upon menthol.

The Presence in Straw of an Aërobic Ferment, Reducing Nitrates.—F. Bréal.—The author has observed a ferment in vegetable débris, which acts in an inverse manner to the nitric ferment of Schlœsing and Müntz. He prepares diphenylamine sulphate for detecting nitrates in the following manner:—He boils pure sulphuric acid so as to expel any trace of nitric acid which may be present. In 100 grms. of the acid, when cold, he dissolves 1 grm. of diphenylamine, previously washed in distilled water and dried. He then adds 25 c.c. of distilled water.

Zeitschrift fur Analytische Chemie.
Vol. xxxi., Part 1.

Gasometric Alkalimetry, and on the Application of Potassium Ferricyanide in Gasometry.—Julius Quincke.—This bulky dissertation, which includes several pages of tables, does not admit of useful abridgment.

Acid Potassium Tartrate as Original Standard Substance for Acidimetry and Alkalimetry.—Prof. Dr. A. Bornträger.—Already inserted.

Volumetric Determination of Phenol.—Dr. R. Bader.—If to an aqueous solution of pure phenol mixed with a few drops of an alcoholic solution of symmetric trinitrobenzol we drop in slowly dilute soda-lye, the liquid remains colourless as long as free phenol is present, but the slightest excess of alkali is recognised by a distinct "onion-red" colour. The solution of trinitrobenzol required is prepared by shaking up repeatedly a knife-point full of pure, symmetric trinitrobenzol (melting-point 122°) with 50 c.c. of absolute alcohol and filtering. It must have only a very faint yellowish colour, and must be preserved in a dark place. For determining phenol in a watery solution he proceeds as follows:—He prepares colourless solution, not too dilute, containing, if possible, not less than 20 grms. per litre; of this 50 c.c. are poured

into a beaker, and there are added 2 to 3 drops (not more) of the trinitro-solution above mentioned. The liquid must remain perfectly clear and colourless. Hereupon normal soda-lye is allowed to fall in drop by drop, whilst the glass is constantly shaken. Towards the end of the reaction the liquid takes a scarcely perceptible yellowish tint. When this point is reached the titration is best continued in the following manner:—2 to 3 drops of soda-lye are added at once, the glass is shaken up, and this is repeated until the reddish-yellow colour produced by the soda no longer disappears. The last 3 drops must be deducted from the total quantity of the normal soda-lye consumed. The end of the reaction is best recognised if we place the beaker during the experiment upon a white porcelain plate. As regards the accuracy of the results they leave nothing to be desired if the solutions of phenol are sufficiently concentrated. In the first attempts the values found are often ½ to ¾ per cent too high. In order to decide whether the homologues of phenol can be titrated alkalimetrically, the author experimented with the three cresols. The values obtained with ortho- and meta-cresol were rather uncertain, whilst in a solution of para-cresol the first drop of soda-lye produced a disturbing yellow colour. The method is not also applicable to pyrocatechin.

Volumetric Determination of Zinc.—L. Blum.—In order to remove manganese, if present, 50 c.c. of the solution to be examined are mixed with a few c.c. of bromine water, then with ammonia and 5 c.c. of Moldenhauer's mixture (which contains in 100 c.c. 5 grms. solid ammonium carbonate, 5 grms. ammonium chloride, and 10 c.c. ammonia). In the precipitate are found the iron, the manganese, and the alkaline earths; zinc and magnesium remain in solution.

A New Thermometer Scale.—F. Salomon (*Zeit. fur Angew. Chemie*).—Already inserted.

The Dispersion of Prism-Spectroscopes. — G. Guglielmo.—Already inserted.

Prevention of "Bumping" in Boiling Liquids.—E. Beckmann (*Zeit. fur Angew. Chemie*).—The author introduces into the heated surface thick pieces of wires (platinum, platinised wire). It is said that in such vessels sulphuric acid can be distilled without danger, and oxidations with alkaline permanganate can be effected without bumping.

Certain Forms of Densimetres.—E. Janisch (*Arch. der u. Math. Phys.*).—In these instruments equal degrees correspond with equal intervals of density.

A Pyknometer for Syrups.—K. C. Neumann (*Zucker Blatt.* and *Zeit. fur Angew. Chemie*).—This instrument has the form of an Erlenmeyer flask, with a high bottom, pressed in conically. In this manner a uniform and rapid cooling is effected.

An Instrument for Determining the Correction in Accurate Readings of the Mercurial Thermometer.—Ch. Ed. Guillaume (*Comptes Rendus*).

Washing-Bottle for Hot Water, Acids, or Ammonia.—A. Friedmann (*Stahl und Eisen*, x., 884).—The flask in place of the short tube is fitted with a three way piece, one end of which is connected with the blast, whilst the other end, when in use, is closed with the thumb.

A Spirting-Bottle.—R. Namias.—The author has constructed a bottle resembling that of D. H. Browne, in which a continuous blast does not need to be kept up with the mouth (*Stahl und Eisen*, xi., 239).

An Apparatus for Determining Melting-Points in a Liquid Bath.—R. Ebert (*Chem. Zeit.*, xv., 76).—For the details of this instrument we must refer to the original.

A Safety-Burner.—M. Lautenschläger (*Zeit. Angew. Chemie*).—A valve is inserted in the gas-pipe, which is held open by an electro-magnet whilst the flame is burning. If the flame is extinguished the current is interrupted and the gas-pipe is closed.

Enamelled Water-Baths with Ring Supports of Enamel.—B. Fischer (*Zeit. Angew. Chemie*).—Already inserted.

A Water Air-Pump Applicable as a Suction-Pump and a Blast.—Max Stuhl.—From a circular; it requires the accompanying illustration.

Water Air-Pumps of Aluminium Bronze.—(*Chem. Zeit.*).—The firm, Ehrhardt and Metzger, of Darmstadt, send out air-pumps of this material.

Improvements in Benzene and Spirit Lamps.—G. Barthel.—The construction of these lamps is shown in the accompanying figures.

The Purification of Mercury.—J. M. Crafts.—From the *Bulletin de la Société Chimique de Paris.*

The Preparation of Lackmoid.—Schaerges (*Schweitz. Wochenschrift Pharmacie* and *Chemiker Zeit.*).—Already inserted.

Separation of Manganese and Zinc.—Paul Jannasch and J. F. McGregory.—Already noticed.

Determination of Phosphorus in Crude Iron, Steel, and Iron Ores.—F. A. Emmerton.—This method is found in a work by A. A. Blair, "The Chemical Analysis of Iron," which we have lately had the opportunity of noticing.

Determination of Phosphorus in Iron and Steel.—Ch. Malet.—From the *Comptes Rendus* and *de la Société de l'Industrie Minerale.*—Already inserted.

Separation of Arsenic and Phosphoric Acids from Mercury, and Determination of Nitric Acid, Chlorine, and Sodium, in Presence of Mercury and Phosphoric or Arsenic Acid.—Konrad Haack. An inaugural dissertation (Meyer and Müller, Berlin).—Already inserted.

Isomeric Determination of Nitrates and Chlorates.—L. L. de Koninck and E. Nihoul.—This paper requires the accompanying figure of the complex apparatus employed.

Reactions for Distinguishing Tannin and Gallic Acid.—J. Napier Spence.—From the *Journ. Soc. Chem. Industry.*

Detection of Saccharin.—D. Vital (*L'Orosi*).—Already inserted.

MISCELLANEOUS.

Occurrence of Vanadium.—According to the *Chemiker Zeitung*, a considerable deposit of vanadium has been found in the Argentinian province, Mendoza.

A Laboratory Device.—Most practical chemists are painfully aware of the unsightly appearance of reagent bottles caused by the drops of the solutions running down the outside and crystallising thereon. This may be prevented by simply painting the rim with melted paraffin. Care should be taken to cover only the side of the lip—none should be put on the upper surface. This can be accomplished most easily by using a *small* hog-hair brush and a wax of low melting-point, such as is used for embedding sections. It will be found that besides preventing the solution trickling down the outside, it enables one to deliver the reagent easily in single drops without resorting to the plan of only partly withdrawing the stopper. *Experto credo.*—R. E. B.

The Atomic Weight of Chrome.—C. Meineke.—The general mean result is Cr = 51·94. This value agrees well with that of Rawson, 52·01, especially if we consider that if reduced to a vacuum it becomes 51·98.—*Zeitsch. fur Anal. Chemie*, xxxi., Part 1.

Process for Purifying Carbon Disulphide without Distillation.—A. Chenevier (*Bull. Soc. de Bord.* and *Chem. Zeitung*).—1 litre of the specimen is mixed with 0·5 c.c. of bromine and left at rest for 3 to 4 hours. The bromine is then removed by agitation with potassa-lye in slight excess or by means of copper turnings. If the liquid is still turbid, it may be rendered perfectly clear by agitation with a small excess of calcium chloride and filtration.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Mine Surveying," by Bennett H. Brough, Assoc.R.S.M.
TUESDAY, 12th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Society of Arts, 8. "English Brocades and Figured Silks," by C. Purdon Clarke, C.I.E.
WEDNESDAY, 13th.—Pharmaceutical, 8.
THURSDAY, 14th.—Mathematical, 8.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Etching on Silver and Steel.—Could any correspondent give me the name of an acid that would eat into the metal without injuring the protecting varnish?—R. H.

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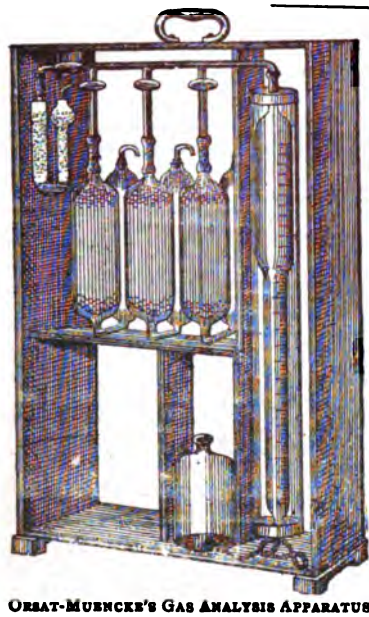

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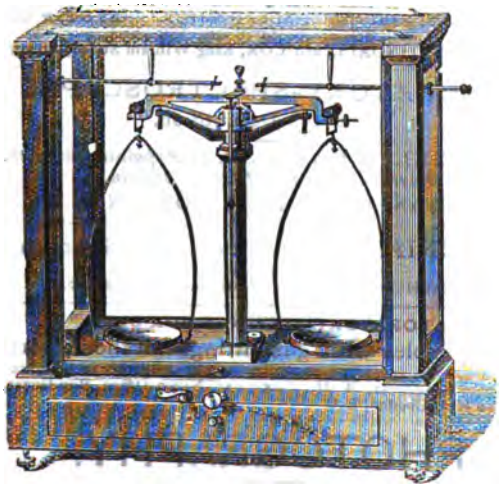

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THE CHEMICAL NEWS.

Vol. LXV., No. 1690.

THE CHEMICAL CHANGES ATTENDING PHOTOGRAPHIC OPERATIONS.

I.—The Theory of Development in Relation to the Essentially Electrolytic Character of the Phenomena and the Nature of the Photographic Image.*

By HENRY E. ARMSTRONG, F.R.S.,
Professor of Chemistry in the City and Guilds of London Central Institution.

No pretension to be even a professional amateur photographer is made by the writer of these lines. At intervals extending over a considerable period he has exposed and developed plates in a conventional and rule-of-thumb manner, but about a couple of years ago an awakening of his photographic conscience took place, and he began to ask himself whether he had any true understanding of what he was doing? Finding that he had not, and that the text-books afforded but cold comfort, he bethought him that he was working in a manner utterly unworthy of a member of that fraternity which seeks to give its meaning to the watchword by which it is led—Science: "Knowledge co-ordinated, systematised, and arranged."

To-night he will attempt but a very general confession of the faith that is beginning to arise within him after much pondering over photographic literature, and after a couple of years of study and experience of the behaviour on development of plates exposed in the field at all seasons, and under a considerable variety of conditions, one chief object in view having been to arrive at the explanation of the controlling influence exercised by the restrainer, and the accelerating effect of alkali.

Thus much by way of preface. A prologue may be added to facilitate the explanation of points of fundamental importance.

In the year 1858 De la Rue and Müller described a new form of voltaic cell consisting of a cylinder of silver chloride cast around a silver wire as negative element opposed to a zinc rod as positive element, placed side by side in a tube containing a solution of a chloride—ammonium chloride being that ultimately preferred. (It is worth while noting that they speak of silver chloride as so poor a conductor of electricity that it may be regarded as an insulator, and that on this account it is necessary that the silver wire around which the chloride is cast should project through it into the solution. On the other hand, it is also noteworthy that even solid silver chloride may be electrolysed, and that directly its temperature is raised sufficiently to make it viscous, it is an exceedingly good conductor). In such a cell the silver chloride remains unchanged until the circuit is completed by joining the zinc and the silver by a conductor of electricity; immediately this is done a current passes, and simultaneously zinc dissolves and silver chloride becomes deprived of chlorine. Although ammonium chloride is used in the cell, in considering the nature of the interchanges it is permissible to assume that hydrogen chloride—one of the constituents of ammonium chloride—is the active agent; for, as will be shown later on, at the same time that hydrogen chloride is being withdrawn from ammonium chloride and used up, hydrogen chloride is being produced and converted into ammonium chloride, and as the two actions balance each other, it is unnecessary to consider them.

Supposing that silver, and not silver coated with silver chloride, were opposed to the zinc in the cell, the latter would dissolve as chloride; but hydrogen would be given off at the surface of the silver. In this case the current would rapidly fall off, the cell would become *polarised* in consequence of back action setting in between the hydrogen coating the silver and the zinc chloride, which would lose chlorine. As it is reversible, the change occurring under such conditions may be written—

$$Zn + 2HCl \rightleftarrows ZnCl_2 + H_2,$$

i.e., the equation may be read either backwards or forwards. In the presence of silver chloride in contact with the silver, this back action or polarisation is prevented, no hydrogen ever being set free, as at the same time that the zinc combines with chlorine from the solution, an equivalent amount of hydrogen combines with chlorine of the silver chloride, and thus the amount of chlorine as ammonium chloride in solution is maintained constant. We therefore may represent the state of affairs in the cell before and after the current passes in the following manner:—

Zinc plate	ClH / ClH	ClAg / ClAg	Silver plate

Cell at rest.

$$= \text{Zinc plate} \mid Zn\begin{matrix}Cl\\Cl\end{matrix} \mid \begin{matrix}HCl\\HCl\end{matrix} \mid \begin{matrix}Ag\\Ag\end{matrix}\left\{\begin{matrix}\text{Silver}\\\text{plate}\end{matrix}\right.$$

Cell in action.

The electrical pressure developed in such a cell—its electromotive force, or E.M.F.—is about 1·05 volt; the theoretical value may be calculated in the following manner:—

It is known from thermo-chemical measurements that the dissolution in dilute muriatic acid ($HCl : H_2O = 1 : 200$) of sufficient zinc to displace 2 grms. of hydrogen would involve the evolution of 34,200 grm.-deg. C. units of heat.

If this amount of hydrogen and the equivalent amount of chlorine were to interact and form hydrogen chloride, 78,640 units of heat would be liberated; while by the interaction of the equivalent amounts of silver (216 grms.) and chlorine, only 58,760 units of heat would be liberated. Consequently, $78,640 - 58,760 = 19,880$ units of heat would be developed if the hydrogen, instead of being liberated, were to reduce silver chloride, and the total heat evolution resulting from the conversion of the zinc into chloride at the expense of the chlorine withdrawn from the silver chloride would be $19,880 + 34,200 = 54,080$ units. The corresponding E.M.F. is found by dividing by 46,000, a constant which need not be explained here; hence—

$$\frac{54,080}{46,000} = 1{\cdot}18 \text{ volt.}$$

The difference between this and the observed value is attributable to the fact that the conditions for which the calculation is made are not precisely those which obtain in an actual cell; probably the zinc chloride is not fully hydrated in the electrical circuit, and the heat of formation of some less hydrated chloride should be taken for the purpose of the calculation.

The extent to which the electrolysis of silver and hydrogen chlorides takes place, *i.e.*, the amount of zinc dissolving and of silver chloride reduced in the cell, depends on the resistance in the electrical circuit, since—

$$C = \frac{E}{R}$$

where C stands for current, E for electromotive force, and R for resistance. This is the well-known *Ohm's Law*; its importance in connection with photographic phenomena has been strangely overlooked.

To apply this law to chemical changes, it has merely to be borne in mind that C may also be taken as meaning amount of chemical change, and it is scarcely necessary to point out that the most exact method of measuring an electrical current consists in determining the amount of

* From the *Journal of the Camera Club*, Conference Number 1892.

chemical change which the current produces by weighing the deposit of silver obtained on passing it through a silver nitrate solution. E, as before, is the electromotive force corresponding to the interchange, and R the resistance, not of the liquid as a whole, however, but of the circuit within which the interchange is effected, which may be quite a different thing, and unfortunately at present is beyond measurement.

It will be noted that the E.M.F. of the silver chloride cell is the sum of two E.M.F.'s, the one developed in the formation of zinc chloride from zinc and hydrogen chloride, the other in the reduction of silver chloride. In any case, in order that action may occur, it is essential that the change, on the whole, be one in which energy is set free; but this is not necessarily the case in all parts of the change when it is resolvable into parts. This is a consideration of primary importance in connection with the theory of development, and may be illustrated by the following examples:—Zinc readily dissolves in diluted sulphuric acid if coupled with a less positive conductor. Copper, however, does not, even if the acid be boiled; but copper dissolves readily enough if oxygen be passed into the heated diluted acid. Thermo-chemical measurement shows that while the dissolution of sufficient zinc to displace 2 grms. of hydrogen from sulphuric acid is attended with a liberation of energy expressed by the number 37,730 if represented in heat units, the dissolution of the equivalent amount of copper could only take place if energy were supplied to the extent of 12,400 heat units; but, as oxygen and hydrogen interact, forming water, with liberation of energy to the extent, measured in heat units, of no less than 68,360 units per 2 grms. of hydrogen, it becomes possible for copper to dissolve in sulphuric acid in presence of oxygen in a circuit containing copper, sulphuric acid, and oxygen, with development of energy equal to 68,360 − 37,730 = 30,630 heat units: *i.e.*, a positive E.M.F. is developed in such a circuit.

In the old collodion wet-plate process, development was effected by means of silver nitrate left adhering to the plate on removal from the silver bath, and a reducing agent such as ferrous sulphate duly restrained by, say, acetic acid. When solutions of ferrous sulphate and silver nitrate are mixed, unless very dilute, a precipitate of silver is soon formed, but the amount precipitated always falls far short of the total amount of silver present, as the interaction is reversible.

$$2FeSO_4 + 2NO_3Ag \rightleftarrows Fe_2(SO_4)_2(NO_3)_2 + 2Ag.$$

Ferrous salt. Ferric salt.

The extent to which silver is deposited depends on the proportions used, the concentration, and the temperature; if the solution be sufficiently dilute and acid be present, no precipitation occurs. The exact function of the acid is not clearly determined, but probably in its presence atmospheric oxygen intervenes, and by acting in conjunction with it and ferrous salt, further promotes the dissolution of the silver, thus rendering reversal complete, *i.e.*, no chemical change is apparent. There can be no doubt that in the liquid the interchanges thus pictured occur within voltaic circuits, and that as no action is observed when acid is present, the algebraic sum of the currents in all these circuits is *nil*. It is to be supposed that on covering an exposed plate with such a solution, the image acts like the silver rod in the De la Rue-Müller cell, silver nitrate taking the place of the silver chloride, and ferrous sulphate that of the zinc rod in the cell: hence the silver is necessarily deposited on the image.

The growth of the image in silver therefore takes place mainly upwards into the solution in the case of a collodion wet plate, and only to a minor extent within the film; it appears probable that the silver haloid particles in the film in contact with the image are but little if at all affected, owing to the superior readiness with which silver nitrate is reduced, and the "weakness" of the developers used. It is very noteworthy that owing to the absence from collodion of "active impurities," its use affords little or no opportunity for the occurrence of changes at points where light has had no action on the film: hence the brilliancy and sharpness of wet collodion pictures.

In considering the alkaline development process of modern gelatin dry plate photography, it would appear to be necessary to distinguish between methods in which the *alkaloid* ammonia, and those in which alkalies, either caustic or carbonated, are used. Even silver bromide is appreciably soluble in ammonia; consequently, in developing with the aid of ammonia, the image is in part formed from silver in solution. The extent to which this takes place depends chiefly on the amount of bromide added as restrainer, one result of adding this restrainer being to precipitate the dissolved silver haloid, or rather to prevent its dissolution by the ammonia. Probably it is to this peculiarity that the marked difference in results obtained by using ammonia and pyro is, at least in large part, attributable; and the same circumstance would favour the formation of an image not wholly composed of silver, *i.e.*, of a species of pigment.

All who have worked with pyro and ammonia know that the picture has properties which distinguish it from those obtained with developers in which ammonia is not used, and that the liability to certain peculiar kinds of fog is special to ammonia developers; this is probably attributable to the conjoint action of the dissolved silver and colouring-matter formed by oxidation of the developer.

When alkalies are used the image grows at the expense of the solid silver haloid with which it is in contact, just as the silver wire in the De la Rue-Müller cell grows at the expense of the silver chloride cast around it. The various developers used, like zinc, are all oxidisable substances; and just as the zinc by combining with chlorine enables the hydrogen of hydrogen chloride to withdraw chlorine from silver chloride attached to the silver wire in the cell, so the developer by laying hold of the oxygen of water enables its hydrogen to withdraw bromine from the silver bromide attached to the image on the photographic plate which has been exposed to light. Taking quinol (hydroquinone) as the type, the interaction may be expressed thus:—

Latent image	AgBr AgBr	H H O	H H $C_6H_4O_2$ ⇐ ⇒
	Silver bromide.	Water.	Quinol.

Before Development.

Latent Ag image Ag	BrH BrH	O H H	C_6H_4O
	Hydrogen bromide.	Water.	Quinone.

After Development.

Viewing the process in this manner the function of the alkali would seem to be to neutralise the acid as it is formed, or rather, to prevent acid ever being formed, thereby preventing a reversal of the interaction which otherwise would take place, owing to the attraction of silver for bromine and of quinone for hydrogen, *on which account the equation given above is written as expressing a reversible change.*

But the remarkable positive influence of alkali in hastening development, and the retarding influence of a bromide, such as potassium bromide, are in no way accounted for in the foregoing explanation.

As regards the alkali, its influence is probably at least in the main due to the fact that a silver haloid in presence of alkali and a reducing agent tends to undergo reduction, the metal of the alkali forming a compound with the halogen while the oxygen of the alkali forms water with the hydrogen of the developer. One of the products of this interchange is the alkali-metal haloid, *and the interchange being a reversible one*, its reversal is promoted by the presence of added bromide, and consequently less silver is deposited when the restrainer is present, thus:—

Image	AgBr AgBr	KOH KOH	$\overset{H}{H}C_6H_4O_2$	⟵ ⟶
		Alkali.		
Image	Ag Ag	BrK BrK	OH_2 OH_2	$C_6H_4O_2$

Provided it be assumed that the latent image is capable of acting in a manner corresponding to that in which the silver rod acts in the silver chloride cell, it is unnecessary to take its precise character into account. Yet to fully understand the relative importance of the various factors operating during exposure and development, it is necessary also to consider the nature of the photographic image. For an able statement and discussion of this and of very many other photographic problems, reference may be made to Meldola's "Chemistry of Photography" (Macmillan and Co.).

It is now generally admitted, Meldola says, that the invisible image is of the same composition as the darkened product of photo-decomposition of a silver haloid, and he inclines to the belief that this darkened product is an oxyhaloid compound of silver.

Mr. H. B. Baker, whose name is familiar to chemists through his remarkable observations on the incombustibility of carbon and phosphorus in dried oxygen, has for some time past been studying this subject with special care, and it may be here stated, on his authority, that when darkened silver chloride is treated with chlorine it gives off oxygen, and that water is formed when it is heated in dried hydrogen; these observations clearly indicate that the darkened substance contains an oxidation product, and confirm Hodgkinson's results, to which Meldola has drawn attention.

But if the arguments adduced in favour of the view that the invisible image is of the same nature as the darkened product be carefully examined, it will be found that they are by no means cogent. One object of this communication is to suggest that probably they are not, and further, that in an ordinary photograph there are perhaps two distinct latent images behaving differently on development, which may be conveniently spoken of as the *blue* and the *yellow* image. It is contended that the blue image is silver, and only the yellow a silver oxyhaloid. The action of light on silver haloids is apparently strictly comparable with that of an electric current—it is *electrolytic*; moreover, the effect of light would seem to be that of a very high electromotive force, and it would therefore overcome great resistance. It may be supposed that when exposed to the mis-called actinic rays—those at the blue end of the spectrum—in contact with a substance capable of appropriating bromine, *i.e.*, a depolariser, such as gelatin, and the products formed therefrom during ripening, silver bromide has its silver liberated. The development of the image thus formed has already been described; such an image would be the absolute counterpart of the silver wire in the De la Rue-Müller cell.

Lower down in the spectrum, in the yellow region, the silver bromide apparently undergoes electrolysis in some occult manner in a circuit which includes oxygen, and while losing some of its bromine takes up oxygen in place thereof.

In anticipation of the objection that if these two actions take place darkened silver haloid should contain both silver and silver oxyhaloid, and that apparently the former is not present in it, let it be remembered that when a moist silver haloid is affected by light, the halogen liberated in the formation of the oxyhaloid will attack the silver which it is here supposed results from the decomposition of the haloid by the blue rays, and will convert it into silver haloid. In a gelatin plate, however, halogen is taken up by the gelatin, &c., and thus the silver would be more or less protected; after a time, the gelatin having become saturated, the silver would tend more and more to become re-halogenised; in fact, it would entirely depend on the length of exposure whether the image consisted of silver and silver oxyhaloid, or only of the latter.

On developing what is known as an over-exposed plate, which presumably is rich in oxyhaloid, the image apparently behaves very differently, according as only alkali is used in conjunction with the developer, or alkali and a bromide. It would seem probable that a silver oxyhaloid would resemble silver oxide in being very unstable, and that in contact with alkali and a reducing agent it would become resolved into silver haloid and silver, thus affording an image in silver, the growth of which, on continuing development, would occur in the manner previously explained. The decomposition of the oxyhaloid, like the change which occurs when solutions of silver nitrate and ferrous sulphate are mixed, would take place, so to speak, with a rush, and the image grow so rapidly that the picture would flash into view. One function of the restrainer is to prevent this sudden change; it would seem that under the conjoint influence of a bromide, alkali, and a reducing agent, the silver oxyhaloid is converted into silver haloid. The extent to which this change takes place, and the rate at which the picture gains in strength, would depend on the amount of bromide present, the relation which obtains between the amounts present of the several substances which act conjointly, the concentration, and the temperature; consequently the picture might, as is the case, be caused to grow at any desired rate.

In a gelatin plate there are always present substances tending to interact with the silver haloid in presence of alkali much in the manner in which silver nitrate and ferrous sulphate interact, and which promote the occurrence of the reduction of the haloid by the alkali and the developer already referred to. Such substances are kept under control by the addition of the restrainer. If, therefore, the development of an over-exposed picture be continued, fog is necessarily produced unless sufficient bromide be added to check the action of the reducing substances in the gelatin. For a similar reason it is desirable to use weak developers with plates which have had a very brief exposure. In such a case the image is so very faint that the difference between the unexposed and exposed portions of the plate is but slight—the value of R in the equation,—

$$C = \frac{E}{R},$$

is very nearly the same in the two sets of circuits. By using a developer which has no appreciable action on the unexposed plate, the latent image is slowly strengthened, and ultimately R is so much diminished that it becomes safe to use a stronger developer.

The development of pressure marks may be explained from the same point of view. Clearly there would be a diminution of resistance in the lines of pressure, and hence on application of the developer, circuits would be formed within the film in these lines, in which action would take place more readily than in the uncompressed parts.

Reversal by means of *thiourea*, with which we have been made familiar by Waterhouse, may also be referred to here. If it be supposed that the latent image is converted into a sulphur compound which is not developable, the action would be confined to the unexposed parts of the film which, sooner or later, always give way under the influence of alkaline developers. Complete reversal would thus be secured.

With reference to the sensitiveness of plates, the explanation at the end of the "prologue" of the influence oxygen exercises in promoting the dissolution of copper in diluted sulphuric acid is apposite. The sensitiser promotes the action of light in a precisely similar manner, it may be supposed; and it is clear that any degree of sensitiveness may be secured, according as the substance associated with the silver haloid, and which acts as depolariser by combining with the halogen thrown off from the haloid under the influence of light, is capable

of contributing more or less of the energy necessary to render the interchange one which would occur without any external E.M.F. being brought to bear.

Judged from the point of view here advocated, it would seem that there can be but very little difference between various developers when used under comparable conditions; at most the variation would arise in the rate at which development would take place. It does not appear probable that the character of the deposit would vary greatly in "grain" or colour. But, since in practice considerable differences are noticed, it is probable that not only in the case of pyro and ammonia, but also in others, the deposit does not invariably consist of silver alone.

In concluding this statement, attention may be called to the great opportunity for research of a by no means difficult character which photography affords. We want experiments made in a great variety of directions, but under much simpler conditions than heretofore adopted; the effects of monochromatic lights, and the influence of various pure substances as sensitisers in association with silver haloids, are especially important subjects to study.

Abney has shown that such a substance as a nitrite stops the action of the yellow rays: we want observations on the effect of such substances. Gelatin plates have been of great service to picture makers, but they are a great bar to scientific progress, as we can never know their exact composition, and we must return to the neutral medium collodion if we wish to gain definite information on matters such as have been referred to. Such experiments, moreover, should have great practical value, as the results may ultimately enable us to largely extend the applications of photography.

THE SCIENTIFIC ALLIANCE.

We have pleasure in calling attention to a movement which has sprung up in New York under this name, and which seems worthy of imitation elsewhere. According to our excellent contemporary *Science*, in March, 1891, six societies engaged in scientific research entered into a confederacy for certain well-defined objects. It is pointedly remarked that:—"The societies do not in any way sink their individuality or surrender any part of the management of their own affairs. Their union is merely in the way of co-operation for the advancement of science and for mutual encouragement, carried out through a central representative body known as the council, having advisory powers only. A monthly bulletin is issued, and is sent to every member, which contains an invitation to the members to attend the meetings of all the societies."

The associated bodies are the New York Academy of Sciences, formerly known as the Lyceum of Natural History; the Torry Botanical Club; the New York Microscopical Society; the Linnean Society of New York; the New York Microscopical Club; the New York Mathematical Society.

It is not too much to say that a similar organisation might be useful in London. The combined influence of such a body might prove a check to the hostile movements alike of the Government and of so-called "advanced thinkers," who are ever on the watch to interfere with research. We need merely refer to the recent ukase touching methylated spirits, in which a foolish step was taken without the courtesy of consulting the Chemical Society and the Society of Chemical Industry. No society on entering such a combination would find its members treated as are the scientific members of our so-called "Literary and Philosophical Societies." Professor Meldola, by the temporary combined action of the London societies connected with the study of natural history, succeeded in defeating a project to lay waste a considerable portion of Epping Forest. It is therefore not too much to hope that by permanent co-operation much good might be done, or at least much intended mischief prevented.

THE SEPARATION AND DETERMINATION OF LEAD, SILVER, AND ZINC IN ORES COMPOSED OF GALENA AND BLENDE.

By EMILE AUBIN.

If we wish to separate and determine the lead, silver, and zinc by the wet way in ores composed of galena and blende, the attack with hydrochloric acid and the use of sulphuretted hydrogen for the separation of these metals renders the operations long and delicate, and the silver cannot be determined with precision. We have thought that it might be preferable to have recourse to fuming nitric acid to form an insoluble lead sulphate and soluble silver and zinc sulphates, which may be separated by filtration. The lead sulphate mixed with the gangue is then taken up and separated from the latter by means of a suitable solvent. Alkaline sodium tartrate, already indicated in analytical treatises, has given us the best results in this operation.

The following is the method which we finally adopted:—In a conical litre flask we act upon 10 grms. of the powdered ore with 50 c.c. of fuming nitric acid, heating the mixture to ebullition and evaporating to dryness on the sand-bath. It is re-dissolved in heat with 20 c.c. of nitric acid at 36° B., and when all the iron has passed into solution, the liquid is made up with distilled water to about 400 c.c. We agitate to re-dissolve the soluble sulphates and the nitrates, and then set the whole aside until the supernatant portion has become clear.

When the lead sulphate has been entirely deposited along with the siliceous gangue, the liquid is decanted through two plain filters previously brought to an exact equilibrium, and then placed one within the other. The deposit is brought upon the filter, completely washed with distilled water, and dried. The weight of the contents is then ascertained by separating the two parts of the filter and placing them on the opposite pans of the balance. Then the contents of the interior filter are let fall into a glass mortar and ground up with 30—40 c.c. of a hot solution of alkaline sodium tartrate at 20 per cent. The lead sulphate dissolves rapidly, and we judge that nothing remains but the gangue by the disappearance of the small white points which indicate the presence of the lead salt. The two filters, one within the other, are replaced in the funnel, and the contents of the mortar, including the insoluble portion, are decanted into the inner one. The filter is washed with distilled water until the filtrate has no longer an alkaline reaction. The siliceous gangue is dried and weighed. The difference of weight between the first and the second weighing represents the lead sulphate obtained from the ore. This weight multiplied by 0·683 gives the lead in the metallic state. This result may easily be checked by re-precipitating the lead sulphate thus dissolved with an excess of sulphuric acid. The precipitate collected and washed upon a double filter, dried, and weighed, is equal in weight to the difference found in the previous determination.

The liquid which contains the silver and the zinc is made up exactly to 500 c.c. Of this we take 50 c.c., representing 1 grm. of ore, and determine the zinc by the ordinary method, *i.e.*, precipitating the iron and alumina with ammonia, filtering, and adding to the filtrate ammonium hydrosulphate in excess to precipitate the zinc, collecting the deposit of zinc sulphide, re-dissolving it in hot hydrochloric acid, filtering, and precipitating the filtrate at the temperature of ebullition with sodium carbonate. The zinc carbonate is collected on a filter, washed, dried, and ignited in a muffle. Its weight multiplied by 0·8025 gives the zinc in the metallic state.

For determining the silver the 450 c.c. of the original liquid are rapidly evaporated down in a capsule to 20 or 30 c.c. It is let cool, when there is formed a crystalline deposit, which is separated by decanting off the super-

natant liquid. Into the limpid liquid we throw 1 grm. pure sodium chloride to precipitate the silver which it may contain. The silver chloride formed is collected on a double filter like that prepared for the determination of the lead, dried, and weighed. The weight multiplied by 0·7527 will give the metallic silver.

The use of the double filter above described permits us to simplify the operation and to suppress the incinerations which, in case of lead and silver, occasion losses or reductions in presence of organic substances.—*Bull. de la Soc. Chim. de Paris*, vols. vii. and viii., No. 5, p. 134.

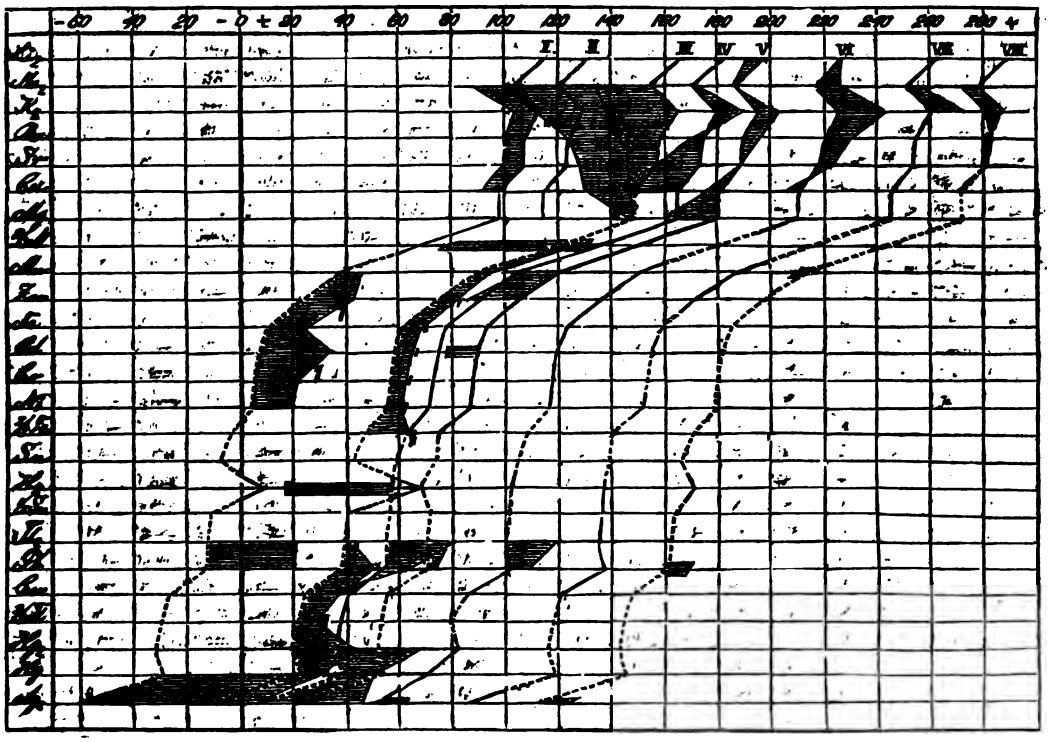
A THERMO-CHEMICAL EQUILIBRIUM.

By P. J. F. RANG.

It is quite impossible to get a good general idea of thermo-chemical data when they are presented in the usual way, in the form of numerical tables; but if we plot these numbers according to graphic rules, it will be easy to grasp and compare a thousand of these facts at once. On the accompanying plate,* each base has mapped its own horizontal line, on which the calories are measured off. Each mapped base is computed to bivalence, and is arranged according to the heat it evolves, while combining with *chlorine* in *aqueous solution*. At the upper part of the plate is the scale of calories.

The heat evolved by the combination in aqueous solution of a certain acid with each base is measured off on the corresponding horizontal line, and all the points obtained in this manner are combined in one zigzag line. The other acids have been mapped in the same manner. All the lines which show the formation heat in aqueous solutions are represented on the plate as strong black lines. In an analogous way we get the hair-fine lines, which represent the formation heats of the anhydrous salts; where such a line has a number printed on it, the corresponding salts are not truly anhydrous, but have so much water of crystallisation, as indicated by the number printed on the line. The space between the hair-fine lines and the strong lines are shaded, and represent the heat of solution. If the shading is inside the strong line, the salt gives off heat when dissolved; and if the shade is on the outside, heat is absorbed during solution.

All the strong lines are strictly parallel, except only in the case of polymerism and hydrogen. This parallelism, when interpreted, represents the thermo-chemical equilibrium, and there is too much in its favour to admit of doubt. The author has therefore extended the black lines by dotted lines to embrace those places where he had no numerical evidence. The errors in the dottings cannot be large, but it is found unsafe to extend the hair-fine lines in the same manner. As in some places we are able to put hair-fine lines opposite the dotted chief lines, we can thus read off the heat of solution of substances which have not yet been dissolved in the wet way; sulphides and hydroxides are instances of this kind.



I. = [M,S,aq.]
II. = [M,S_2,H_2,aq.]
III. = [M,O,aq.]
IV. = [M,Br_2,aq.]
V. = [M,O,SO_3aq.]
VI. = [M,O_2,N_2O_4,aq.]
VII. = [M,O_2,$2SO_2$,aq.]
VIII. = [M,CO_3,aq.]
M = the metal computed to bivalence.

If the accompanying plate be examined closely it is seen to embrace two classes of precipitates:—1. Salts that give off heat whilst precipitating; these salts are compressed in the act of precipitation, and heat escapes from them in the same manner as oil does when pressed

* The Plate is made up with the aid of the tables in M. M. Pattison-Muir's "Elements of Thermal Chemistry," printed in 1885.

out of linseed. 2. Salts which, whilst crystallising out from the mother-liquor, do not give off any heat: some of these salts take up heat whilst they are crystallising—the carbonates are instances of this kind. Precipitation; here is a kind of congelation or coagulation, and the atoms of carbon, silicon, and near-related elements impart such a property to some of their salts.

Before I end this paper, may I take the opportunity of fervently asking investigators to direct their attention to *uric acid*: for, according to Martignon (Chem. News, vol. lxii., p. 12), this acid must have very wonderful properties: the important part it plays in the animal organism points to this same fact.

Wimmerby, Sweden, March 21, 1892.

A QUICK AND RELIABLE METHOD FOR THE DECOMPOSITION AND ANALYSIS OF FERROCHROME.

By H. N. WARREN, Research Analyst.

The analysis of ferrochrome is in itself no simple task, to say nothing of its previous decomposition. Samples containing high percentages of chromium are only slightly affected after long boiling with aqua regia,—hydrochloric or any other simple acids being entirely inadequate. True, a slow and imperfect decomposition may be brought about by fusing with acid potassium sulphate, and is often quickened by the addition of borax, but the results thus obtained are useless, insomuch that the precipitates afterwards thrown down all contain large quantities of borates. The method, which is here described in brief, consists as follows:—

Having introduced a weighed quantity of the finely powdered substance into a convenient size flask, a sufficiency of strong H_2SO_4 is next added, and the action aided by a gentle heat. A copious evolution of SO_2 is almost at once evolved, and the heat is then increased until volatilisation of the H_2SO_4 is plainly perceptible; the whole of the ferrochrome is thus in the course of a few minutes brought into solution. To the solution thus obtained is added a few drops of HCl, the solution diluted to a known quantity having been previously filtered from the trifling carbonaceous residue, and an aliquot portion titrated with standard $K_2Cr_2O_7$ in order to ascertain the percentage of iron, a further portion being precipitated as chromic and ferric hydrates. From these data the percentages of both chromium and iron may be readily obtained; or if manganese or aluminium is considered worth allowing for, the precipitates are of course dealt with accordingly. A more complete and accurate analysis may be thus arrived at than by any hitherto known method. Analysts of iron works please take note.

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THE PROPERTIES OF AMORPHOUS BORON.

By HENRI MOISSAN.

Amorphous boron, when pure, is a powder of a light maroon colour, which soils the fingers and may be agglomerated by strong pressure. Its specific gravity is 2·45. It is infusible at the temperature of the electric arc. If kept at a temperature bordering upon 1500°, in an atmosphere of hydrogen, it increases in density and is slightly agglomerated, though without becoming consistent.

Its electric conductivity is very slight; to measure it a pastille of boron is compressed between two plates of copper placed in a glass tube of known diameter. The resistance was then determined and the specific resistance α was deduced from the formula $R = \frac{\alpha l}{s}$. We have found for $l = 8{\cdot}5$ m.m., and $s = 2{\cdot}27$ m.m.c., R = 300 megohms, whence $\alpha = 801$ megohms.

In the air boron takes fire at the temperature of 700°. If strongly heated in a test-tube, and then thrown up into the air, it produces brilliant sparks. If heated in a current of oxygen it burns with a light so intense as to be insupportable. In a darkened room this incandescence appears green, but produces few chemical rays, thus it cannot be substituted for magnesium for photographic purposes.

In these various combinations the boron is not burnt entirely, for the layer of boric acid produces sets bound to the reaction. It combines with sulphur at 610° with a very beautiful incandescence; there is formed boron sulphide, which is decomposed by water with a production of hydrogen sulphide.

Selenium reacts at a higher temperature and without incandescence; there is produced boron selenide, which is decomposed by water with the disengagement of hydrogen selenides. Tellurium may be melted among amorphous boron without combination.

Boron takes fire in an atmosphere of dry chlorine at the temperature of 410°. The incandescence is very intense and boron chloride distils over. If the amorphous boron contains a small quantity of carbon or of carbon boride, a slight black residue is left in the boat. At the same time there are deposited in the tube traces of magnesium chloride and ferric chloride. Bromine combines with incandescence amorphous boron at about 700°, yielding boron bromide.

Bromine water slowly attacks amorphous boron at the ordinary temperature. If the boron contains magnesium boride the attack is much brisker, and there is a distinct evolution of heat. Pure boron is attacked more rapidly by a mixture of bromine, and of an aqueous solution of potassium bromide.

In a gas-furnace at 950° amorphous boron is not attacked by the vapour of iodine; combination does not even take place in a porcelain tube heated to 1250°. Iodine water has no action upon boron. Boron does not combine directly with antimony except at a very high temperature. At 900° in a current of pure dry nitrogen, boron yielded mere traces of a nitride after several hours. At 1230° combination takes place much more easily.

The vapour of phosphorus does not react upon amorphous boron at 750°; it is the same with arsenic; antimony does not combine even if kept at its point of fusion. Carbon and silicon strongly heated do not appear to unite with boron. Still, under the action of the arc in an atmosphere of hydrogen, boron can combine with carbon, producing a carbon boride. The alkaline metals may be distilled over amorphous boron without producing a trace of combination. Magnesium, on the contrary, yields a boride at dull redness.

Iron and aluminium combine with boron only at high temperatures, whilst silver and platinum unite with it more readily. We are continuing in detail the study of the action of boron upon the metals.

Acids react energetically upon boron. At 250° sulphuric acid is reduced to sulphurous acid. Monohydrated nitric acid, in presence of an excess of boron, combines with incandescence. Phosphoric anhydride is reduced at 800°, with the liberation of phosphorus. Arsenious and arsenic acid are reduced at 800°, with the formation of a ring of arsenic. A hot solution of iodic acid liberates iodine in contact with boron. A mixture of boron and crystalline iodic acid, if gently heated, becomes incandescent, with the formation of intense vapours of iodine. Chloric acid in solution is reduced to chlorous acid.

The hydracids react less readily. Gaseous hydrofluoric requires to be heated to dull redness in order to act upon boron, and it is then split up into hydrogen and boron fluoride. Gaseous hydrochloric acid reacts only at a

bright red heat; its saturated solution has at 0° no action upon amorphous boron. Gaseous hydriodic acid reacts upon pure boron only at a temperature between 1200° and 1300°. Sulphurous acid gas is reduced by boron at a temperature below redness, the products being boric acid and vapours of sulphur.

Watery vapour does not react upon boron below redness, but as soon as incandescence has been reached at any point, the decomposition ensues with violence, boric acid being formed and hydrogen escaping.

At a temperature bordering upon 1200° carbon monoxide is reduced by amorphous boron, boric acid being formed and carbon deposited.

Melted silica is reduced by boron at the temperature of a good forge. Boron, if heated to dull redness in a tube of glass traversed by a current of nitrous oxide, becomes incandescent, yielding boron nitride and boric acid. Under the same conditions of temperature nitric oxide produces no result.

Metallic oxides are reduced more readily by boron than by carbon. If we heat, *e g.*, in a glass tube a mixture of cupric oxide and boron, the evolution of heat is so great that the glass melts immediately. Stannous oxide, litharge, oxides of antimony and of bismuth, are reduced at once if gently heated, and the entire mass becomes incandescent.

Lead dioxide, if ground up in a mortar with boron, detonates violently. Ferric oxide and cobalt oxide are reduced at a bright red heat. The alkaline-earthy oxides are not attacked. Potassium hydroxide, if melted in contact with amorphous boron, produces a violent liberation of hydrogen.

The avidity of boron for oxygen may be demonstrated by means of a mixture of amorphous boron, sulphur, and potassium nitrate. This is a real gunpowder, which deflagrates below a dark red heat. We may also show this avidity by letting fall upon melted potassium chlorate some particles of amorphous boron. Combustion ensues with a dazzling light. This is a fine lecture experiment.

The action of boron upon certain metallic fluorides is very energetic. With the alkaline and alkaline-earthy fluorides there is no reaction at a bright red heat. Zinc fluoride is reduced by boron at dull redness, yielding boron fluoride. Lead fluoride is reduced in the same manner, displaying a lively incandescence. If the quantity of boron is rather large the mixture deflagrates. Silver fluoride reacts in the cold, on simple contact in a mortar, with incandescence and detonation.

Boron does not attack the alkaline and alkaline-earthy chlorides. Zinc and lead chlorides do not react at redness. Mercurous chloride mixed with boron yields about 700° boron chloride and vapours of mercury. Lead, zinc, cadmium, and copper iodides, if heated with boron in a glass tube, are not reduced, though the tin and bismuth iodides are readily reduced.

Potassium and sodium sulphates, if melted in a glass tube, are reduced by boron at a dull red heat. The incandescence is very intense, and there is produced an alkaline sulphide. Calcium and barium sulphates are reduced in the same manner, with incandescence. A part of the sulphur is volatilised, and there remains a metallic sulphide.

Although the affinity of boron for oxygen is very great, we may keep boron in a bath of an alkaline nitrate melting at 400° without any reaction. The attack begins only at the moment when oxygen begins to be evolved. With melting potassium nitrite the decomposition is attended with a great display of heat and light.

Sodium carbonate is reduced by boron at dull redness with a lively incandescence. For potassium carbonate the reduction is effected at a higher temperature. Calcium and barium carbonates are not decomposed. The arsenites and arseniates, as also the chromates, are reduced at dull redness, with incandescence.

We indicate a curious action which amorphous boron exerts upon a certain number of metallic solutions. Amorphous boron reduces a solution of potassium permanganate in the cold, and the decolouration is complete on slightly raising the temperature. It reduces solutions of ferric chloride to the ferrous state. A solution of silver nitrate is reduced, with a production of very fine crystals of metallic silver. Palladium chloride is reduced in a few minutes at the common temperature. With platinum chloride the reaction commences in the cold, and is accelerated by a slight rise of temperature. If a few particles of boron are projected into a solution of gold chloride, reduction in the cold is instantaneous.

Boron combines less readily with the metals than with the non-metallic elements. It has a strong affinity for fluorine, chlorine, oxygen, and sulphur. It is a more powerful reducing agent than carbon and silicon, for at a red heat it expels oxygen from silica and carbon monoxide, and it will probably permit reductions more easily than those hitherto obtained with carbon.

Its action upon the metallic oxides easily reducible by carbon is very violent; it reacts very easily with a great number of salts, and it combines directly with nitrogen only at a very high temperature.—*Comptes Rendus*, cxiv., p. 617.

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Section B.—Chemistry and Mineralogy.

Address by the President,
WILLIAM M. HAMLET, F.I.C., F.C.S.,
Government Analyst, N.S.W.

(Concluded from p. 175).

The economical production of caustic soda would enable other wet process to be used, such as Ellershausen's wet process for the extraction of the precious metals from zinc ores. These latter give rise to grave difficulties in many parts of New South Wales, notably at the Barrier Ranges; in many cases the zinc is lost to the community for want of a suitable process of extraction. The method I refer to is one which can be economically worked in connection with the caustic soda manufacture. The zinc ore is mixed with 25 per cent of galena, if it does not already contain that quantity of galena, and after being crushed, is put in a reverberatory furnace and heated to a red heat, when from 35 to 50 per cent of caustic soda (the crude refuse from the soda works) is added). The whole mass fusing, the galena readily gives up its sulphur to the soda, and metallic lead is produced, which, with the gold and silver, sinks to the bottom, the sulphides of iron, copper, and zinc remaining in the slag. The lead is drawn off and cupelled, and the slag, on exposure to the air, rapidly crumbles to powder owing to the caustic soda present, which is afterwards removed by lixiviation, and can be used over again, while the metallic sulphides can be treated by the usual methods. The ore should previously be concentrated to remove quartz, as the soda would be wasted in forming silicate of soda and not recoverable. The late Mr. Wilkinson, my lamented friend, who drew my attention to this interesting process, held the opinion also that the ores of Broken Hill, Moruya, and Castle Rag could be successfully treated in this way.

In addition to the many forms of chlorinating processes, there remains for me to mention another, the principle of which is that the sulphur present in many sulphide ores may be subjected to a particular degree of oxidation in a reverberatory furnace, whereby the soluble sulphate of silver is formed; this is afterwards separated out by leaching with hot water, as already described; the silver being separated as metal, while the copper and iron compounds are left as insoluble oxides. This process, known as Ziervogel's, is particularly well suited to argentiferous pyrites carrying from 10 to 40 ozs. of silver per ton.

Another process of wet extraction has been lately patented by Dr. Storer, of Sydney, and Mr. Marsh, of Broken Hill, which may be briefly described as follows:—The ore is roasted in a reverberatory furnace along with limestone, the mass lixiviated with water, the zinc precipitated by magnesia as hydrate, which on filtration yields nearly pure zinc oxide.

Closely associated with the different processes I have brought before you, as well as with smelting operations generally, is the nature of the fuel and its suitability for metallurgical work. Mr. J. C. Mingaye, Assayer to the N.S.W. Government, has undertaken a thorough examination of the coals and cokes available in New South Wales, and finds them nearly equal in every respect to those of Europe and America, the exceptions being in the refractory nature of the ash of some specimens,—a defect, however, which is partly compensated for by their greater freedom from the undesirable elements phosphorus and sulphur.

The phenomenon of solution is, therefore, of world-wide interest, as we see its application in our arts, industries, and manufactures, as well as in the every-day acts of our lives. And all these changes, velocities, rotations, vortices, and precessions, even if we do not as yet perceive them, have been going on under our very eyes from the beginning; they are still going on in our laboratories and workshops, as well as in the great arena of nature. The truth is, that things constantly before us become so commonplace as to no longer awaken our interest as they did in the freshness of youth. Who has not observed the mixed feelings of awe and wonder when some friend comes, it may be for the first time in his life, to witness some natural phenomenon in a laboratory? Do we not find that such an one thus coming fresh upon the scene, untrammelled and free from preconceived notions, sets us thinking by some original and unanswerable question? There are not wanting among us some who talk of the narrowing tendency of the pursuit of Chemistry as a discipline of the mind. Such a view is totally at variance with fact and experience, since the great issues dependent upon a knowledge of Chemistry, and the enlarged conception of the universe gained by its study, places it in the front rank as an instrument of great educational value, and one best fitted to bring forward (*séducé*) habits of observation and reflection.

One has but to think of the enthusiasm of a Liebig, a Faraday, and a Hofmann, and of the indomitable truth-seeking spirit which animated them, their sufficient reward being the inward satisfaction of having worked out, at first hand, an imperishable fact direct from Nature. To such as these comes the promise of the poet—

> "Thy mind
> Shall be a mansion for all lovely forms;
> Thy memory be as a dwelling place
> For all sweet sounds and harmonies."

Even such a mind as that of M. Renan has expressed the regret that he did not dedicate his life to chemistry instead of Oriental languages. Sir Henry Roscoe recently gave a reminiscence of the talented chemist, Dumas, who, after having declared that he had seen every phase of life—student, teacher, minister, professor, senator—but no work had he been called upon to perform had been so satisfactory, or had been looked back upon with such pleasure, as that of carrying on original work; and, he says, "If I had to live my life over again, I would not relinquish my quiet laboratory pursuits for all the splendour and influence of Court favour, or the turmoil and rewards of political life."

The advance of our science may be ascribed, not so much to the rewards offered by wealth, as to the disinterested love of truth on the part of the worker; for what man can pursue the even tenor of his way upon research work with the feverish spirit engendered by some pecuniary prize dangling before his eyes? The advance of Science may, moreover, be attributed to the greater freedom of the person, and to the full freedom of thought that can be focussed at will upon everything relating to objective truth.

It was possible with our forefathers not to inquire, but it is fortunately impossible to stem the tide of free inquiry that, like the ether around us, pervades every thinkable subject. We remember, however, that the lives of our forefathers were overshadowed by the gaunt and chilling arm of Authority, which effectually barred the road to knowledge. *Tempora mutantur;* and with our freedom comes the intellectual growth and the desire to ascertain the truth as it may be revealed to us by the infinitely great and by the infinitesimal molecule. Let us not close our minds to the appreciation of the mutual relationship existing between the divisions of science known as Chemistry, Physics, and Astronomy; for what we know is as nothing to what we do not know and what still remains to be known. This may be a truism—sometimes it is half doubted. To me it seems like the literal truth, and that if we narrow our views to already half-conquered territory only, we shall be false to the men who won our freedom, and treasonable to the highest claims of Science.

And now, with the end in view, I feel conscious of having only touched the fringe of one phase of the all-absorbing subject of the nature of this beautiful universe; but, so far, you will, I think, agree with me in saying that the study of matter in its manifold aspects is not only worthy of our best energies, but full of promise for the future. The hard mechanical conceptions, accompanied by the dread born of an unreasoning superstition, formerly held regarding Nature, the irreverent and loose talk about "brute matter," and of dead motionless matter, is passing away. The "dead" matter is quickened, and is alive with movement. What was once taken for absolute rest and immobility is in a state of high tension and rapid motion, yet always in perfect harmony and in keeping with the orderly progress of the universe. Whether we peer out into the ethereal depth inlaid with suns, or whether we observe a crystal of potassium iodide dissolving in water, we have rolling worlds in the one case and the eddying molecule in the other, the gamut of the Universe being complete, from the protean carbon atom to the remotest so-called fixed star. Must we not, therefore, feel that the contemplation of such perfection of structure and such majesty of motion claims both our admiration and attention, and must lead us to recognise that in all around us we have—

Vox Dei in rebus revelata.

As with Lucretius, the gaze of the philosopher of the day is again centred upon the atom. The question still asked is, What are the atoms?

> Ageless units in the amplitude of space,
> Outlasting the ravage and the wreck of Time:
> Now in a dewdrop distill'd from a rosebud;
> Here in a crystal; there poised in a sphere
> Evolving from fire-mist new worlds for the future
> To vibrate anew the great clarion of Life.
> These—these are the atoms.

THE FRACTIONAL ANALYSIS OF SILICATES.*

By F. W. CLARKE.

In the course of some investigations upon the constitution of the natural silicates it was found that in most cases the empirical formulæ were capable of interpretation in various distinct ways, leading to different structural expressions of equal probability. In some instances there was available evidence, by means of which it was possible to choose between alternative formulæ; the final decision resting sometimes upon the association of minerals in nature, and sometimes upon the alterations which they undergo. Such data, however

* *Journal of the American Chemical Society*, xiii., No. 10.

are not always readily available, and even at their best they only establish presumptions in place of giving satisfactory proof. It became necessary, therefore, to seek for new data of an experimental kind, which should be analogous to the data used by the organic chemist in fixing the constitution of carbon compounds, and by their means to put the problem upon a more satisfactory footing.

Two difficulties were evident from the start. First, the impossibility, in the present state of our knowledge, of measuring the molecular weights of the silicates; and secondly, the lack of plasticity in the material under investigation. The first difficulty is still insurmountable; but the second is less formidable than it appeared at first, and the experiments presently to be described open up a feasible line of attack upon the outworks of the problem. The results are appearing in detail in a series of mineralogical papers by E. A. Schneider and myself, and only an outline of the chemical methods need be given in this communication. So far, the minerals studied belong mainly to the mica and chlorite groups, with a few other magnesian silicates like talc, serpentine, and olivine as accessories; and it remains to be ascertained whether the methods applicable to these compounds will fit other cases equally well. Theoretically, the outlook is favourable, but difficulties may exist which cannot be foreseen.

Of the minerals heretofore examined all but one, olivine, contain water. This may represent water of crystallisation, acid hydrogen, or hydroxyl in union with basic atoms, and the first problem is to discriminate between these several possibilities. To begin with, the relative stability of the water in each molecule gives a clue to its character; water of crystallisation being easily expelled at comparatively low temperatures, and water of constitution being more tenaciously retained. In each case, therefore, the temperature of dehydration was roughly ascertained; every mineral being heated to constant weight first at 100°, then at 250°, 300°, and finally at a full red heat. Whenever ferrous iron was present the total water was also determined directly, and so the errors due to possible oxidation during ignition were avoided. Studied in this way the vermiculite micas, kerrite, jefferisite, and protovermiculite, gave exceedingly suggestive results, each mineral corresponding to an ordinary mica, plus three molecules of water of crystallisation, and with the alkaline metals of the original mineral equivalently replaced by hydrogen. Furthermore, the crystalline water fell sharply into two parts; two molecules being expelled at 100°, and the third being given off below 250°. Thus a mica having the composition $Al(SiO_4)_3Mg_3KH_2$ would yield by hydrous alteration a vermiculite represented by the formula $Al(SiO_4)_3MgH_3 + {}_3H_2O$, to which latter compound kerrite approximately corresponds. In the true micas and chlorites the water does not seem to break up into separate fractions upon mere heating, and, being stable up to or near redness, is to be regarded as constitutional.

Up to this point the work done presents no particular novelty, and involves no new modes of procedure. The fractional determinations of water, however, have a direct bearing upon subsequent experiments, and clear the ground for work of a more troublesome kind. Having evidence before us regarding the amount of hydroxyl in a given silicate molecule, the next problem is to determine its distribution and character. It may be united with silicon, representing unreplaced hydrogen of the original silicic acid, it may be combined with magnesium in a univalent group —Mg—OH, or it may be linked with aluminum as =Al—OH or —Al=$(OH)_2$. In its broadest aspect the problem is still far from complete solution, but at one point it has been attacked with some success, as follows:—

All of the silicates above mentioned as studied by us, except talc, are easily decomposable by aqueous hydrochloric acid. By dry hydrochloric acid gas, however, they are differently affected, and the differences seem to be due to the character of the hydroxyl. Each silicate in turn was weighed out in a platinum boat, and heated to constant weight at a temperature of about 400° in a stream of the thoroughly dried gas. The temperature, it must be noted, is one at which the water of constitution was still retained by the minerals. Olivine, which *contains no hydroxyl*, was practically unattacked, although the aqueous acid decomposes it with great ease. Talc, the true micas, and the vermiculites, were not acted upon, or at most very trivially. Serpentine and the chlorites, however, were strongly affected; and from them, after the reaction, water extracted considerable amounts of magnesium chloride, in which the magnesia was estimated. In serpentine and ripidolite about one-third of the magnesia was thus removable; or, in other words, the magnesia was separated into two fractions, which presumably were differently combined. In these minerals the group —Mg—OH is almost necessarily assumed in any attempt to interpret their structure; and the amount of magnesia taken out as chloride was roughly proportioned to the quantity required by the simplest theory. That is, it seems probable that —Mg—OH in a silicate is converted by dry hydrochloric acid into a chlorhydrin group, —MgCl, the latter, by subsequent action of the gas being split off altogether as chloride, $MgCl_2$. This is the simplest explanation of the phenomena; although the nature of the reaction is by no means proved, and a good deal of investigation into it is still necessary. At all events, as regards the magnesium silicates of the groups studied, the new reaction appears to be a legitimate test for —Mg—OH, even though it may not be strictly quantitative. When action takes place the group is almost certainly present; when there is little or no action, its absence may fairly be assumed.

(To be continued).

NOTICES OF BOOKS.

Chemistry in Space. From Professor J. H. Van 't Hoff's "Dix Années dans l'Histoire d'Une Theorie." Translated and Edited by J. E. Marsh, B.A. Oxford: Clarendon Press, 1891.

Strictly speaking, structural formulæ are intended not to show the respective positions of the various elements which make up a molecule, but merely the relations existing among them. Still, in the minds both of their advocates and of those who reject them, there has lurked half unconsciously a notion that these graphic formulæ could or should to some extent shadow forth the constitution of a molecule could we view it with the requisite magnifying power. Hence, we have occasionally heard complaints concerning the folly of representing bodies of three dimensions upon a plane surface. The avatar of "chemistry in space," of the attempt to exhibit the manner in which the atoms of compounds are really grouped together, may therefore justly be hailed as a step in the right direction. At the same time, it is a most difficult step, which without extreme circumspection will expose us to the risk of going astray. For the present, the chemists who have initiated this advance are exceedingly cautious. They have not made any wide-reaching assumption, but have merely taken up the hypothesis of the "tetrahedral carbon atom." The theory in question originated, as we are told, independently and simultaneously in France and in Holland. M. J. A. Le Bel, in November, 1874, read a memoir before the Chemical Society of Paris on "The Relations which Exist between the Atomic Formulæ of Organic Bodies and the Rotatory Power of their Solutions." He reminded the Society of the correlation between molecular dissymmetry and rotatory power. Prof. Vant 't Hoff published, in the Dutch language, in September, 1874, a "Treatise on a System

of Atomic Formulæ in Three Dimensions, and on the Relation between Rotatory Power and Chemical Constitution." Here, therefore, identical conclusions seem to have been reached substantially by following the same train of thought. This pamphlet soon appeared in a German version, and, as it is here remarked, received two diametrically opposite criticisms from two chemists of recognised eminence. The two authorities in question were Wislicenus and Kolbe. The critique of Kolbe was not merely hostile, but contemptuously hostile. His motive was a doubt of the possibility of ascertaining the true arrangements of the atoms in a molecule, or, at least, of knowing positively whether our interpretation was correct or otherwise.

The author shows that this theory throws a valuable light upon the phenomena of isomerism.

In the chapter on the monatomism of compounds we find that, according to Pasteur and Le Bel, an inactive compound may be converted into one either dextro-rotatory or lævo-rotatory by the action of organisms.

We hope that "chemistry in space" will be thoroughly and carefully worked out. It has already obtained recognition so far that it no longer need fear the "conspiracy of silence."

The Year-Book of Science. Edited, for 1891, by Prof. T. G. Bonney, D.Sc., LL.D., F.R.S. Small 8vo., pp. 473. London and Melbourne; Cassell and Co., 1892.

We have here an annual built on almost the same lines as a defunct publication of very similar title; but the present work is a very decided advance on its fore-runner. Its subject-matter is gleaned, not from stray newspaper paragraphs—canards, distortions, or at best exaggerations of the truth—but from writings of specialists, as found in the Transactions of leading Academies and Societies, or from established scientific journals. Hence its contents are trustworthy.

The editorial preface contains much that is interesting. Says Dr. Bonney: "The increasing technicality of the terminology employed is also a serious difficulty. It has become necessary to learn an extensive vocabulary before a book in even a limited department of science can be consulted with much profit." This is too true. It has often struck us that one great advantage which the German student has over his English contemporary is that the former encounters technical phraseology built up out of his native tongue, whilst the latter has to grapple with a terminology intended to be Greek. It is humiliating to find an eminent official *savant* in one moment protesting against the predominance of classical studies in our colleges, and in the next engaged in the wholesale coinage of technical terms which only a Greek scholar can hope to understand. Odd-toed or even-toed are quite as precise as perissodactylate and artiodactylate, and very decidedly more concise.

The editor and his coadjutors seem to have experienced some difficulty in deciding how much ground should be covered. However this may have been, they seem to have come to a happy decision. The boundary-line between Science and technical applications seems to us distinct enough. If engineering and photography were admissible, why not medicine? Mathematics may possibly yet come to be regarded as a method, rather than as a science. The admission of metaphysics would be gravely to be deprecated.

As regards the various subjects, it seems to us that too great space has been conceded to organic chemistry, which is generally interesting only to the specialist.

Under "Animal Biology," we miss a sub-section on taxonomy and animal geography, corresponding to the sub-section "Systematic and Geographical Botany." Such a department would doubtless prove exceedingly interesting to the educated outsider. Among the subdivisions of the section on "Biology (Botanical)," we find one headed "Morphology and Biology of Plants." We feel curious to know the exact sense in which the term "biology" is here to be taken. It cannot be meant as a synonym for physiology, according to the usage of some Continental authorities, since there follows a subsection on vegetable physiology.

The section on Meteorology is exceedingly interesting. We particularly notice the alarming conclusion arrived at in *Ciel et Terre*—which certainly agrees with our own observations—that a cold winter has never been followed by a very hot summer, and that in the great majority of cases the summer following a severe winter has been cold. Hence we have a poor prospect for the ensuing season.

The work altogether should find a good opening, not merely among intelligent outsiders, but should prove a boon to scientific men, since they find themselves more and more in the position of "outsiders" in every department but their own.

A New Course of Experimental Chemistry, including the Principles of Qualitative and Quantitative Analysis; Being a Systematic Series of Experiments and Problems for the Laboratory and Class Room. By John Castell-Evans, F.I.C. London: Thomas Murby.

The author admits in his preface that if he had simply added another to the long array of chemical text-books much ingenuity would be needed to justify the proceeding; but he considers that "something was wanting" which no existing manual or collocation of manuals could supply; that there was "something radically wrong in the usual way of teaching chemistry, &c." The something wanting he has in this book endeavoured to supply. We certainly cannot undertake the prolonged task of comparing all the existing manuals with that of Mr. Castell-Evans, and of pointing out if and where they fall short, and if, and how, the present author has avoided their errors. We may, however, venture to say that three at least of the existing short text-books—we names of which, of course, we may not mention—have done, or are doing, good service. Further, unless our memory is greatly at fault, not a few of the authors of other manuals, manualettes, guide-books, handbooks, and text-books assert, each in turn, that the existing works are defective, and that there is pressing need for improvement. The "guiding idea" of the present work is excellent. It is designed "not to furnish the student with a knowledge of chemistry, but to help him to acquire that knowledge in the most thorough and scientific manner." Nothing could be better. Mr. Castell-Evans has sought to produce "not a collection of facts, but of methods and means of discovering facts, and of drawing conclusions from them." If the author teaches chemistry in this spirit, his pupils may be congratulated.

We are further told that "since this work has been in the publisher's hands, the British Association has appointed an unusually strong committee to inquire into the methods adopted for teaching chemistry." Surely the answer to such an inquiry would not be very far to seek. Let them give in their formal protest against the examinational system, with its appendages of "payment by results" (falsely so-called), and of the "grant-earning standpoint." Here, we are sorry to find, the author does not go with us in rejecting the system which tends to assimilate Britain with China. An accompanying table is said to "cover the honours degree in chemistry of the London University, Oxford and Cambridge Local, and South Kensington Examinations. We would earnestly beg the author to reflect whether our present system of studying with reference to some examination or other is not a fatal mistake.

Appointment.—Mr. F. J. M. Page, B.Sc., F.I.C., has been appointed to the Chair of Chemistry and Physics at the London Hospital rendered vacant by the death of Dr. C. Meymott Tidy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académi des Sciences. Vol. cxiv., No. 13, March 28, 1892.

Attempt at a Theory of the Production of the various Vegetable Galls.—A. Laboulbène.—The chief cause of the production of galls consists in liquids emitted by galligenous animals and plants.

Temperature of the Sun.—H. Le Chatelier.—The author ascribes to the sun the effective temperature of 7600°, the error in either direction not probably exceeding a thousand degrees.

On a Lamp without Flame obtained with Coal-Gas.—F. Parmentier.—If a thin extended platinum wire is rendered incandescent with a Bunsen burner, or any other burner not producing a luminous flame, and the gas is suddenly turned off and not turned on again until the wire has fallen below dull redness, the platinum returns very rapidly to dark redness and then to bright redness. If the wire has been placed at about the half height and outside the zone where the blue cone is formed when the jet is kindled it always re-lights itself. If the wires instead of being stretched out are rolled up in close spirals we obtain anew a bright incandescence of the platinum and a re-ignition of the gaseous mixture. With thick platinum wires the experiment rarely succeeds.

The Fixation of Iodine by Starch.—G. Rouvier.—Starch may fix iodine without it being necessary to take for 4 atoms of iodine 1 mol. of hydriodic acid or of an iodide.

The Determination of Fluorine.—Ad. Carnot.—This paper will be inserted in full.

Bromised Aldehyds and Acetones resulting from the Action of Bromine upon the Alcohols of the Fatty Series.—A. Etard.—The action of bromine upon the alcohols of the fatty series enables us to obtain in abundance the bromo-aldehyds and acetones, the preparation of which has hitherto been impracticable.

Propylamines and Some of their Derivatives.—F. Chancel.—In order to obtain pure propylamine it is necessary to use oxalic ether, which gives dipropyloxamide. On pouring oxalic ether into a mixture of about equal volumes of monopropylamine and water, there is immediately a precipitate of dipropyloxamide. But if the oxalic ether is added by small quantities, and the temperature is prevented from rising, there are formed monopropylamine oxalate and propyloxamate. Propylamido-acetic acid is prepared by the action of monopropylamine upon ethyl bromacetate.

Certain Reactions of the Isomeric Amido-Benzoic Acids.—Oechsner de Coninck.—Orthoamidobenzoic acid dissolves with the aid of heat in ordinary nitric acid, giving a garnet-red solution, then the tint rapidly turns to a dark brown. The meta- and para-isomers give similar colourations, but the para-compound is most resistant against nitric acid. Fuming nitric acid strongly attacks the ortho-amidobenzoic acid in the cold; the solution is a deep brownish-red. If distilled water is added it becomes red by transmitted, and reddish-brown by reflected light. It soon becomes turbid. The meta-acid is also strongly attacked, forming a red solution; on dilution with distilled water the solution becomes of an orange-red both by reflection and by transmission, and there is no turbidity. The author has in like manner examined the reaction of the three isomeric acids with aqua regia, with hydrochloric acid, dilute and concentrated, and with sulphuric acid.

Two Fluorhydrines of Glycerin.—Maurice Meslani.—Gaseous allyl fluoride reacts with ease upon bromine, giving rise to a dibromfluorhydrine, $C_3H_5FBr_2$. With chlorine it yields under the same conditions a dichlorhydrofluorhydrine, C_3H_5F,Cl_2. These compounds are liquids, endowed with great stability, and do not attack glass even at temperatures much above their own boiling-point.

Speed of the Decomposition of the Diazo-Compounds.—J. Hausser and P. Th. Müller.—A mathematical paper, not admitting of useful abstraction.

Revue Universelle des Mines et de la Metallurgie. Series 35, Vol. xvi., No. 1, October, 1891.

New Process for the Determination of Soluble Chlorides, Bromides, and Iodides.—L. L. de Koninck and E. Nihoul.—In 1886 M. Quantin published a method for the determination of sulphates based upon the reaction between these salts and barium chromate. Under certain determined conditions we obtain—

$$M_2SO_4 + xBaCrO_4 = BaSO_4 + (x-1)BaCrO_4 + M_2CrO_4$$

M representing a monovalent metal. The barium sulphate and the excess of barium chromate are eliminated, and the soluble chromate formed is then eliminated. As the quantity of the latter formed is molecularly proportional to that of the sulphate, this determination enables us to calculate the weight of the sulphate contained in the substance under analysis. It seemed to us that an analogous method might be applied to the chlorides. It is known that silver chromate reacts rapidly with the alkaline chlorides to form silver chloride and a soluble chromate. If we treat a neutral solution of chloride with an excess of silver chromate we have—

$$2MCl + xAg_2CrO_4 = 2AgCl + (x-1)Ag_2CrO_4 + M_2CrO_4,$$

the quantity of soluble chromate formed being proportional to that of the chloride. It is only necessary to remove by total or partial filtration the excess of insoluble chromate, and to determine the chromate contained in the liquid to obtain by calculation the quantity of chloride to be determined. For the determination of the soluble chromate formed the authors use the method of Zulkowski improved by Grismer, *i.e.*, by means of hyposulphite with the intervention of potassium iodide and in presence of sulphuric acid. For preparing silver chromate they weigh two portions of silver nitrate and neutral potassium chromate, both pure, so that there may be 7 parts of silver nitrate to 4 of chromate. The two products are dissolved separately, and the two solutions are mixed, washed by decantation, and preserved under water in the absence of light. Potassium dichromate must not be used. The process consists in agitating with the solution of chloride an excess of silver chromate, filtering, washing, and determining in the filtrate, to which are added the washing-waters, the soluble chromate formed by the iodometric method. To 1 atom of chlorine there correspond 3 atoms of iodine, and consequently 3 mols. of hyposulphite. As regards the precautions necessary we recommend:—1. To use only silver chromate perfectly pure, and which has been preserved under water in the dark. 2. To operate only with perfectly neutral solutions. If the solution is *slightly* acid it may be neutralised by means of pure calcium carbonate. If the solution is alkaline it must be neutralised with dilute nitric acid, an excess of which may again be neutralised with calcium carbonate. 3. The known precautions for the iodometric determination of chromate must also be taken. An excess of alkaline sulphate should not be taken. The determination of bromides and iodides is effected exactly in the same manner as that of the chlorides. The precipitate of silver bromide or iodide often passes through the filter, but this fact does not interfere with the titration of the chromate.

Carbon Monoxide and Nickel, and its Application to the Metallurgy of this Metal.—L. Mond.—The substance of this paper is to be found in the CHEMICAL NEWS for August 28, 1891.

Zeitschrift fur Analytische Chemie.
Vol. xxxi., Part 1.

Detection of Isocholesterine.—E. Schulze (*Zeit. fur Phys. Chemie.*—Already inserted.

The Saponification of Fats and Esters.—A. Kosel and K. Obermaier.—This paper will be inserted at an early opportunity.

Determination of Tannin.—S. J. Hinsdale.—From the CHEMICAL NEWS. See also R. Koch in *Dingler's Journal* (280, 141), and Whitely and Wood (*Journ. Soc. Chem. Ind.*).

Examination of the Air at Breweries, &c., for Micro-Organisms.—P. Lindner (*Wochenschrift fur Brauerei*).—Already inserted.

Determination of Salicylic Acid in Beer and Similar Liquids.—H. Elion.—About 100 c.c. of the sample, after the addition of a little sulphuric acid, is shaken out with 2 or 3 vols. of ether. The salicylic acid is then withdrawn from the ether with small quantities of water, to which a little caustic alkali is added, and the aqueous solution thus obtained is neutralised with hydrochloric acid. In presence of salicylic acid this liquid gives the well-known colouration with ferric chloride.

Determination of Alumina in Wine.—L. Hôte.—From the *Comptes Rendus*.

Examination of Spirits.—The official regulations adopted by the Swiss Government.

Detection of Preparations of Cochineal in Sausages.—A. Klinger and A. Bujard.—The sample, finely minced, is extracted in a boiling mixture of equal parts of glycerin and water. If a preparation of cochineal is present the solvent takes a decidedly red colour. When cold it is filtered, and if but little colouring-matter is present additional 20 grms. of sausage are digested with the filtrate. The clear solution is examined spectroscopically.

Determination and Examination of Fats.—A collection of notes on oils and fats which will be abstracted by opportunity.

On Weighting Leather.—W. Eitner (*Der Gerber*).—Already inserted.

Action of Potassium Fluoride upon Anhydrous Chlorides. Preparation of Anhydrous Nickel and Potassium and Cobalt and Potassium Fluorides.—C. Poulena.—M. Güntz in his thermic researches on the compounds of fluorine with the metals, has shown that in the action of hydrofluoric acid upon potassium chloride the thermic maximum always corresponds to the fluorhydrate of a fluoride of the formula KF,HF. Hence the author concluded that in this manner there might be obtained anhydrous double fluorides of the formula KF,MF. In this manner a number of such compounds have been obtained. He describes at present two, the potassium-nickel and the potassium cobalt fluorides. The former body is slightly soluble in water, scarcely soluble in methylic and ethylic alcohols, and insoluble in amylic alcohol, in benzene, and in oil of turpentine. Its specific gravity is 3·27. Hydrofluoric acid dissolves it in the cold, as also do hydrochloric and nitric acids, its solubility in which increases with the temperature. Sulphuric acids attacks it very slowly at common temperatures, but more rapidly in heat, converting it into sulphate, with elimination of hydrofluoric acid. Ammonia, in the presence of this salt, gradually takes a violet-blue colour. If heated in presence of air this fluoride is converted into nickel oxide, green, and well crystallised, and into potassium fluoride, which escapes. It is reduced by hydrogen at a red heat. Potassa and the alkaline carbonates in fusion convert it into nickel oxide and alkaline fluoride. Cobalt potassium fluoride, CoF_2KF, behaves with solvents in the same manner as the nickel compound. Its specific gravity is 3·22.—*Comptes Rendus*, cxiv., No. 13.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"The Chemist."—I have *The Chemist*, vols. 1 to 7, 1840-46; vols 1 to 4, New Series, 1849-53; vols. 1 to 5, New Series, 1853-58. Were there any volumes published for 1847, '48, and '49? I have in several cases seen bound up with vol. 5, 1857-8, the first two numbers of vol. 6. Is this merely a coincidence? If not, I should like to know how much longer the journal ran.—J. CUTHBERT WELCH.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Meteorological, 7.
——— Microscopical, 8.
THURSDAY, 21st.—Chemical, 8.
FRIDAY, 22nd.—Quekett Club, 8.

NEW PUBLICATIONS.

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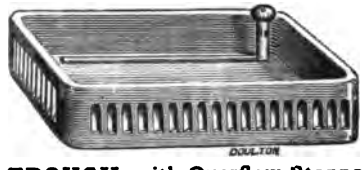

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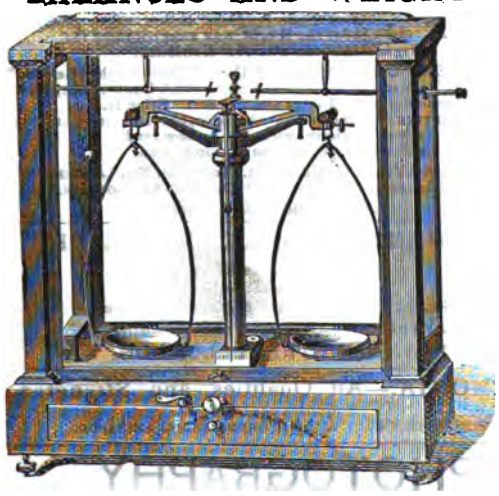

FIG. 52.

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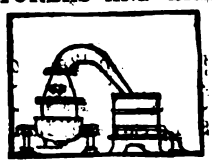

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THE CHEMICAL NEWS.

Vol. LXV., No. 1691.

ON THE APPLICATION OF A HYDROGEN FLAME IN AN ORDINARY SAFETY-LAMP TO THE DETECTION AND MEASUREMENT OF FIRE-DAMP.*

By FRANK CLOWES, D.Sc. (London),
Professor of Chemistry, University College, Nottingham.

In a former paper (*Roy. Soc. Proc.*, vol. l., p. 122) an apparatus was described, in which the appearance of the "cap" over the flame of a safety-lamp could be observed and measured when the lamp was exposed to definite mixtures of air with methane or fire-damp. The relative sensitiveness of different forms of lamp, and of different flames, when they are applied to the detection and measurement of "gas," was thus readily ascertained. It was stated that the flames of colza oil, rape oil, mixed oils, benzoline, methylated spirit, and hydrogen had been experimented upon; and that the non-luminous flames producible by benzoline, alcohol, and hydrogen far excelled the more or less luminous oil flames in their power of indicating low percentages of inflammable gas or vapour in the air. It was further found that the delicacy of the test was much increased by grinding the inner surface of the back of the glass cylinder of the lamp, so as to destroy its reflecting power.

Ashworth's modified benzoline safety-lamp was especially referred to as an efficient lamp both for lighting and for gas-testing. The brilliant illuminating flame gave a forward light equal to one miner's candle. When it was reduced in size by drawing down the wick it became blue and non-luminous; and when it was viewed in this condition against the ground glass surface, or, better still, against the dead-black background produced by smoking the interior of the lamp glass at the back, a distinct flame cap, 7 m.m. in height, was seen in air containing only 0·5 per cent. of methane or fire-damp. The height, density, and definition of the cap over this flame were found to increase pretty regularly as the percentage of "gas" in the air was augmented. The efficiency of this lamp for lighting and testing is thus placed beyond doubt.

In continuing the experiments described in the former paper, however, a comparison of the "caps" produced by the flame of this lamp with those produced by a small alcohol flame and a small hydrogen flame showed that the latter flames were more sensitive as gas indicators than that of the benzoline lamp. Thus, when an alcohol and hydrogen flame, each 10 m.m. in height, were introduced, together with the small blue benzoline flame, into the testing chamber, which was filled with air containing 1 per cent. of coal-gas, flame caps of the following dimensions were obtained:—

Hydrogen	27	m.m.
Alcohol	19	,,
Benzoline	7·2	,,

It is true that the benzoline flame employed in this experiment was much smaller than the two other competing flames. But it must be remembered that the benzoline flame is *necessarily* small when it is employed for gas-testing, since, if its dimensions are increased, it becomes luminous, and renders the pale "cap" invisible. And one of the principal advantages of the alcohol and hydrogen flames consists in their remaining non-luminous, even when they are made of large dimensions; the greater surface and higher temperature of their larger flames producing, therefore, much larger and more visible "caps" than is possible with a small benzoline flame.

It will be seen from the results of the experiment just described that the hydrogen flame has the advantage over the alcohol flame in the dimensions of the "cap" which it yields. But by prolonging the test, another advantage of the hydrogen flame over its rival was ascertained. The two flames were allowed to burn side by side in the chamber, charged with air containing 1 per cent. of coal-gas for over thirty minutes. Throughout this protracted test both the hydrogen flame and the "cap" above it remained unaltered in size and appearance. The alcohol flame and its "cap," however, steadily diminished in size; after five minutes the height of the cap had fallen from 19 m.m. to 12·5 m.m., and after another interval of five minutes the height of the cap was reduced to 6·5 m.m.; and thirty minutes after the beginning of the experiment the flame was spontaneously extinguished. This result seems to indicate that the alcohol flame is much more sensitive to the influence of the presence of products of combustion, and to deficiency of oxygen, than the hydrogen flame is: the difference is possibly due to the much smaller quantity of oxygen required by the hydrogen flame for its combustion.

Alcohol Lamps.—The possibility of producing large and distinct "caps" when testing by means of an alcohol flame for low percentages of "gas" in air was taken advantage of by G. Pieler in 1883 to produce the most sensitive form of safety-lamp for gas-testing yet invented. The Pieler lamp is a large Davy lamp, burning alcohol from a circular wick, which yields a large flame, 30 m.m. in height. When the lamp is used for testing even the feeble light of this flame is shielded from the eye, so as not to interfere with the perception of the "cap." Experiments with this lamp in known percentage proportions of "gas" and air have been described by several observers, and their results were fully confirmed by a series carried out in the test-chamber. The "caps" obtained were as follows:—

0·25	per cent. of methane	gave a	30	m.m. cap.
0·5	,,	,,	65	,,
0·75	,,	,,	75	,,
1·00	,,	,,	90	,,

Indeed, the flame of this lamp is so sensitive that when the proportion of methane in the air reaches 1·75 per cent. the "cap" touches the top of the gauze of the lamp, and with a somewhat higher percentage of "gas" the enlarged "cap" completely fills the interior of the gauze.

Practical men, who have used this lamp, seem to feel some doubt as to its perfect safety in the mine. But their main objection is that the alcohol flames is non-luminous, and accordingly a second lamp must be carried for lighting purposes when the Pieler lamp is employed for gas-testing.

Attempts have been made to obviate the inconvenience of carrying two lamps by constructing a safety-lamp with two reservoirs. One of these would contain oil, and the other alcohol. Each would be supplied with a wick in the ordinary way. By raising or lowering one wick or the other a luminous oil flame for lighting purposes, or a non-luminous alcohol for gas-testing, should thus be obtained at will within one and the same lamp; the flame being passed from one wick to the other, as may be required. Practical difficulties arose in the use of this composite lamp, which have prevented its adoption.

Hydrogen Lamps.—Pieler was aware of the advantage secured by employing a hydrogen flame for gas-testing. Owing to the difficulty, however, of adapting a hydrogen supply to a portable safety-lamp, he recommended that samples of air from the mine should be brought to the surface, and tested by a hydrogen flame burning from a

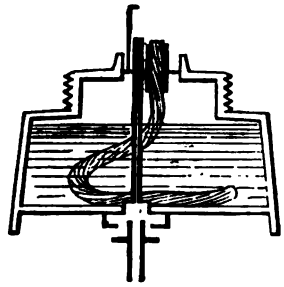
* A paper read before the Royal Society.

chemical generator, the apparatus being a fixture in a testing-room situated near the pit's mouth.

Since, however, hydrogen gas is now obtainable at small cost, compressed in light steel cylinders, it has been found possible to furnish a supply of the gas to a jet inclosed in an ordinary safety-lamp.

The lamp is so constructed that oil or benzoline may be burnt in the ordinary way from a wick when the lamp is to be used for lighting purposes, the wick being drawn down so as to produce a non-luminous flame, and this yielding caps in gas-testing when proportions of gas exceeding 3 per cent have to be looked for. When proportions of gas less than 3 per cent are to be looked for and estimated the hydrogen gas is introduced by a metal jet fixed close to the wick; the gas at once kindles. The wick is then drawn down until the oil flame is extinguished, and the cap is looked for over the hydrogen flame. A cap is easily seen over this hydrogen flame when only 0·25 per cent. of gas is present. When the illuminating flame is required the wick is again pushed up, and kindled by the hydrogen flame. The supply of hydrogen may then be withdrawn. The oil flame and the hydrogen flame are thus made to supplement one another in the same lamp in gas-testing.

The hydrogen is at present supplied from a small steel cylinder, 3 inches in diameter by 8 inches in length, and weighing 4 pounds. The cylinder when fully charged contains 4 cubic feet of hydrogen. This supply lasts for many tests, since when the flame is kept burning continuously at the ordinary height of 10 m.m. it consumes only 1 cubic foot of gas in about four hours. A regulator may be adapted to the neck of the cylinder, but it has been found that a very delicate valve in the neck of the cylinder serves to adjust the stream of gas with ease without the intervention of any regulator.



The cylinder is slung in a leather case by a strap across the shoulder. A flexible tube from the nozzle of the bottle connects the bottle with a little flanged metal nozzle, and this can be attached to an opening in the bottom or side of the oil reservoir of the lamp. The hydrogen is thus supplied to a copper tube of fine bore, which passes through the reservoir, and terminates on a level with, and close by, the top of the wick. Before the hydrogen is fed into the lamp it is gently turned on and allowed to sweep the air out of the flexible tube; connection is then made with the lamp, and by careful adjustment of the valve of the bottle the flame is made of the required size. The aperture in the lamp for introducing the hydrogen is closed by an automatic valve when the hydrogen is not in use.

Several series of measurements of "caps" were made over the hydrogen flame of this lamp in the testing chamber. The flame was adjusted to a height of 10 m.m. by viewing it through a metal diaphragm, containing a hole 10 m.m. in diameter, and held outside the lamp; or by making its tip level with the top of an upright wire fixed inside the lamp, and near the burner. A glass cylinder extra height (90 m.m.) was fitted into the Ashworth lamp, and a dead-black background was produced by smoking a broad strip of the internal surface of the internal surface of the back of this glass with a wax taper. The blackened glass not only gave a surface against which pale caps were easily seen, but the dead surface prevented perplexing reflections giving ghosts of the true flame. The percentage of methane in the air in these experiments varied from 0·25 to 3, and the following heights of cap represent the average of a large number of fairly concordant readings:—

With 0·25 per cent. of methane,				17	m.m. cap.
,,	0·5	,,	,,	18	,,
,,	1·0	,,	,,	22	,,
,,	2·0	,,	,,	31	,,
,,	3·0	,,	,,	52	,,

In the 3 per cent mixture the tip of the cap disappeared in the opaque metal cylinder of the lamp above the glass. The hydrogen flame therefore became useless for measuring higher percentages, unless it was much reduced in size; but at this point the oil flame is competent to take up the indications with certainty. When very low proportions of gas are to be tested for the size of the hydrogen flame may be increased with advantage, as is described below; but no observer could fail to see the smallest cap mentioned above with the 10 m.m. flame.

The advantage of increasing the size of the hydrogen flame when small percentages of gas are being looked for is shown by the results of the following experiments made by exposing the hydrogen safety-lamp in air containing 1 per cent and 0·5 per cent of coal-gas respectively: the height of the cap being noted in each mixture when the hydrogen flame was first 10 m.m., and then 15 m.m. in height.

Per cent.	M.m. cap.		M.m. cap.	
1 gas ..	27 (flame 10 m.m.)	..	50 (flame 15 m.m).	
½ ,, ..	23 ,, ,,	..	38 ,, ,,	

Attention is directed in the above statement to the *height* of the cap alone, but as a matter of fact, its change in general appearance is also very noticeable as the proportion of gas is increased. Very careful observation of the hydrogen flame in air free from gas serves to detect a slender and very pale cap. When the gas in the air reaches 0·25 per cent the cap becomes broader and pale grey in colour, but is still indefinite in outline, especially at its summit, and is seen only *above* the hydrogen flame. As the proportion of gas increases the flame becomes strikingly sharp and pointed in outline, distinctly bluish-grey in colour, and gradually broadens and extends down the sides of the hydrogen flame, finally enclosing it altogether and encircling the jet. At the same time, the hydrogen flame itself is constantly growing in every dimension, gaining in luminosity and acquiring a rosered tip. It is well to have watched the above changes in the test-chamber, and to have become familiar with the appearance of the hydrogen flame in different percentages of gas before the flame is used for gas-testing.

The use of the hydrogen flame for gas-testing has the advantage of rendering possible the employment of a non-luminous flame, which can be immediately adjusted to any convenient size; not only may the size of the cap be thus increased at will by enlarging the flame, but it is possible to avoid the risk of losing the flame in the lamp, which is incurred by drawing down the wick very low when an oil flame is made use of for gas-testing.

The Solution of Antimony Chloride in Saturated Solutions of Sodium Chloride.—Antimony chloride, $SbCl_3$, in contact with water, undergoes a partial decomposition which transforms it into oxichloride, SbOCl,—a decomposition which obeys the general laws formulated by H. Sainte-Claire Deville. Without changing the reaction set up by the water, without modifying any of the general data which allow it to be classed among phenomena of dissociation, it is possible to displace the part of the acid, substituting for it a salt such as sodium chloride, and to obtain a solution of antimony perfectly neutral.—*Bull. Soc. Chim. de Paris*, No. 2, 1892.

ON THE

OCCLUSION OF HYDROGEN BY LEAD.

By JOHN SHIELDS, Ph.D., B.Sc.

SINCE the introduction of secondary batteries by Planté and Faure, a large amount of work has been done by various observers in order to obtain a clearer insight into the various changes which occur during the charging and discharging of the cells. The question of the occlusion of hydrogen by metallic lead, which has often been asked, has also received a good deal of attention, but the answers furnished by the different observers unfortunately do not agree. It is the object of this paper to bring together the evidence for and against the occlusion of hydrogen by lead, and to supplement it by some additional experiments.

Frankland (*Proc. Roy. Soc.*, xxxv., p. 67) was perhaps the first to institute experiments to decide this question. He proceeded by reducing red lead electrolytically, and examining the spongy substance which was thus obtained, in order to see whether it consisted solely of metallic lead or contained hydrogen associated with it in any way. The reduced mass was placed in a combustion tube and heated until the lead melted, but no measurable quantity of hydrogen was given off.

Graham found that palladium, which had served as the negative electrode during the electrolysis of dilute sulphuric acid, and which thereby becomes charged with a large quantity of hydrogen, possesses the property of reducing potassium ferricyanide to potassium ferrocyanide, potassium chlorate to potassium chloride, &c. Gladstone and Tribe ("The Chemistry of Secondary Batteries," p. 48), have applied this method to the spongy lead, and as the result of several experiments they found that the amount of hydrogen associated with the reduced lead was almost inappreciable.

Several authors have simply assumed, with no experimental evidence whatever, that hydrogen is occluded by spongy lead. The same assumption has also been made by Drzewiecki and Streintz, but these gentlemen have adduced facts which were believed to justify it. Drzewiecki (*La Lumière Electrique*, xxxv., 290) measured the potential difference between the two poles of his secondary battery and found it to be 2·15 volts. He then measured the difference of potential between each of the poles and a piece of clean lead which he immersed in the electrolyte, and obtained 0·2 and 1·7 volt respectively. From these observations Drzewiecki concludes that the difference in behaviour of plain and reduced lead is due to the absorption of hydrogen by the latter. That a difference does exist cannot be doubted, but it by no means follows that this is due to occluded hydrogen, especially as no other facts have been brought to light which justify this conclusion, whilst a great many tend to prove the reverse.

Streintz (*Wied. Ann.*, xxxviii., 355) has also described an experiment which was supposed to prove the occlusion of hydrogen by reduced lead. If a completely charged cell is disconnected from the charging current and closely observed, one can see bubbles of gas rising from both plates. The gas which is given off at first from the peroxide plate soon ceases; according to Gladstone and Tribe it is oxygen, probably produced by the action of peroxide of hydrogen on the peroxide of lead. The evolution of gas from the lead plate, however, continues for weeks and even months; it has been shown to be hydrogen, and in its production Streintz finds an argument for the hypothesis that it is occluded by the lead and afterwards slowly given off. The other possibility, namely, that it is produced by the action of the dilute sulphuric acid on the spongy lead, he rejects, as he says he would have been able to detect white sulphate of lead by means of the eye had any been formed. Now Thomson (*Thermochem. Untersuchungen*, iii., 335) has shown that lead belongs to that class of metals which decomposes water, and Gladstone and Hibbert (*Phil. Mag.*, August, 1890, and January, 1891), have performed an experiment similar to that described by Streintz, but not content with the look of the plate they analysed it afterwards and found it to contain about 85 per cent of sulphate of lead; moreover, the sulphate of lead formed in secondary batteries, as Frankland has pointed out, is not perfectly white in colour. So that the hydrogen which is given off from the reduced lead is without doubt one of the products of the action of lead on dilute sulphuric acid, lead sulphate being formed at the same time.

This view has also been confirmed by Cantor (*Monats. fur Chemie*, xi., 444), who found that the amount of hydrogen which was disengaged was exactly equivalent to the sulphuric acid which was "fixed" during the disengagement. By means of a weighed cell in which the peroxide plate was replaced by a platinum electrode, he also succeeded in showing that no hydrogen was occluded by the lead. He estimated the total amount of hydrogen contained in the cell before charging and compared it with what was given off in the gaseous state during charging together with what remained behind in the electrolyte, and found that the two amounts agreed within the range of experimental error, which proves that no hydrogen could have entered into association with the lead electrode.

Thoma (*Zeit. fur Phys. Chem.*, iii., 91), has shown that iron wire occludes ten times its volume of hydrogen at the ordinary temperature, and according to the experiments of Bellati and Lussana (*Atti. R. Ist. Ven.*, i., Series VII., p. 1173), hydrogen diffuses through an iron plate which is used as the negative electrode on electrolysing dilute sulphuric acid. Before applying this method to lead it was thought advisable to repeat some of the experiments of the Italian physicists, and so obtain confirmation of this very remarkable fact. A strong glass funnel with a stem about a metre long was therefore taken and a side tube fused on near the top. A piece of clean sheet iron such as is used in making telephones was supported on a porcelain filter plate and made to close the funnel air-tight by means of sealing-wax run in round its edges. The tube was then dipped into a trough of mercury alongside of another barometer, and after the air had been pumped out, the side tube was sealed up. We had thus two barometers, one of which was closed at the top by means of an iron plate, standing side by side, so that differences of level could easily be measured. After it was quite certain that the iron plate was sealed on perfectly air-tight, the funnel was filled with very dilute sulphuric acid, and the iron plate connected with the negative pole of a battery; a coil of platinum wire suspended in the acid served as the positive electrode. A few minutes after the circuit was completed the column of mercury began to descend. The following table, in which column I. gives the time in minutes, and column II. the depression in millimetres, will give some idea of the rate at which the hydrogen diffuses through the iron.

I. Min.	II. M.m.	I. Min.	II. M.m.
0	0	105	16·0
10	1·3	133	20·8
20	2·0	160	25·4
25	3·7	228	36·7
30	4·5	307	48·5
40	6·0	375	60·1
57	8·8	520	80·5
71	10·9	1360	169·5
87	13·4	1745	196·5

Bellati and Lussana have shown that the vacuum on the lower side of the iron plate is not the cause of the passage of the hydrogen through it, and that it merely magnifies the volume of the hydrogen and makes the diffusion more easily visible. With a modified form of apparatus they have succeeded in obtaining pressures up to several atmospheres.

	Pt.		Pd.		Fe.		Cu.		Au.		Ag.	
	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	P.c.
Initial P.D.	1·20		1·014		0·164		0·712		1·096		0·959	
P.D. after polar., 0 min.	0·438		0·189		0·260		0·164		0·425		−0·243	
1 ,,	0·891	59·5	0·685	60·2	0·233	27·2	0·710	99·8	0·942	72·0	+0·781	84·8
2 ,,	0·945	66·2	0·726	65·0					1·000	85·6	0·850	90·5
3 ,,	0·979	71·0	0·740	67·0					1·028	89·9	0·864	91·8
4 ,,	0·986	71·8	0·740	67·0					1·041	91·6	0·891	95·9
5 ,,	0·997	73·1	0·750	68·1	0·225	36·5			1·055	93·8	0·918	96·8
10 ,,	1·003	74·0	0·754	68·6	0·222	39·6	0·712	100·0	1·090	99·0	0·946	98·6
30 ,,	1·025	77·0	0·781	71·8	0·214	47·9	0·712	100·0	1·096	100·0	0·959	100·0

	Pb.		Sn.		Zn.		Al.		Ni.		Carbon.	
	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	P.c.
Initial P.D.	+0·178		0·231		−0·397		0·069		0·685		1·233	
P.D. after polar., 0 min.	−0·329		−0·341		−0·413		−0·329		0·301		−0·027	
1 ,,	+0·110	85·0	−0·041	52·5	−0·397	100·0	−0·055	69	0·658	96·0	+0·864	71·0
2 ,,	0·178	100·0	+0·014	57·2			+0·123	113	0·740	114·0	1·028	83·6
3 ,,			0·096	76·3			0·178	127	0·740	114·0	1·082	88·2
4 ,,			0·203	95·1			0·178	127				
5 ,,			0·223	98·6			0·164	124	0·726	110·8	1·096	89·2
10 ,,	0·178	100·0	0·223	98·6			0·137	117			1·123	92·2
30 ,,	0·178	100·0	0·223	98·6	−0·397	100·0			0·713	107·0	1·200	97·6

Having verified the experiments of Bellati and Lussana we substituted a thin lead plate for the iron one, but no depression of the mercury took place. This is exactly what we should expect of a metal which does not occlude hydrogen, were it not for the very remarkable fact that neither platinum nor palladium, both of which are known to occlude gases, permit of the passage of hydrogen through them under the same circumstances. Experiments with plates of these two metals carried out in precisely the same way, although allowed to go on for fourteen days in order that they might become fully saturated with hydrogen, showed no depression of the mercury.

On applying the method which Helmholtz and Root (*Monatsber. d. Berl. Acad. d. Wiss.*, 1876, p. 217) employed to show the occlusion of hydrogen by platinum to lead, a negative result was also obtained.

The rate at which the potential difference between a polarised plate and a non-polarisable electrode falls off, affords another method for investigating whether a given metal occludes hydrogen or not. The metal to be examined was dipped into a vessel of water to which a few drops of sulphuric acid had been added, and the potential difference between it and amalgamated zinc in a solution of zinc sulphate measnred. It was found that this measurement could not in general be made at once, as differences amounting to several hundredths of a volt were frequently observed; after the lapse of about twenty or thirty minutes, however, the readings remained constant. A platinum plate acting as an anode was then placed in the liquid, and the metal under examination polarised for an hour,—in some cases for three or four hours,—and the current interrupted. Measurements of the potential difference between the various metals examined and zinc in a solution of zinc sulphate, were made at the moment of breaking the battery circuit, and afterwards at frequent intervals with Prof. Ostwald's modification of the capillary electrometer and a suitable compensating apparatus. The following table shows some of the results which were obtained. The first column gives the potential differences, and the second the percentage fall of the polarisation.

A cursory examination of the table enables one to see that the substances examined may be divided into two main groups: first, that in which the potential difference falls off very slowly; and second, that in which the original potential difference is regained after a few minutes; and these two groups, leaving carbon out of account, contain respectively the metals which do, and those which do not, occlude hydrogen. When hydrogen occurs only superficially on a metal it quickly becomes oxidised, and the difference of potential due to it rapidly disappears; but when the hydrogen has entered into association with the metal, this process of oxidation occupies a much longer time, owing probably to diffusion, and consequently the original potential difference is regained only after the lapse of several hours.* Nickel and aluminium show the anomalous behaviour which has often been noticed by other observers; it is highly probable that neither of them was pure. In the case of zinc almost no polarisation effect was obtained. This agrees with the fact that very nearly the same electromotive force is required in order to separate zinc and hydrogen from their compounds, as Le Blanc (*Zeitsch. fur Phys. Chem.*, v., 467; viii., 299) has shown.

In conclusion, it is evident from the above table that lead belongs to that group of metals which does not occlude hydrogen, and as all the other evidence is in agreement with this fact, we are compelled to reject the hypothesis, which is sometimes advanced and which has recently been defended by Streintz and others, that hydrogen is occluded by lead and plays an important part in the chemistry of secondary batteries.

It is my pleasant duty to thank Prof. Ostwald for his kindness and help during this investigation.

Leipzig, December, 1891.

Postscript.

Since the above was written another paper by Neumann and Streintz has appeared in the *Monats'hefte fur Chemie*, xii., 642, the object of which is to prove the assumption which was made in a former paper, viz., that hydrogen is absorbed in large quantities by lead. Now the evidence which has just been shortly reviewed tends to prove the reverse of this; at the same time it ought to be carefully borne in mind that no attempt has been made to show that *absolutely no hydrogen* is absorbed by lead, for it is a well known fact that almost all substances possess the property of condensing gases and vapours on their surface. All that is maintained is, that lead practically occludes no hydrogen, and that it does not play the important part in the chemistry of secondary batteries which has often been ascribed to it.

In order to form an idea of the quantity of hydrogen which they assumed to be absorbed we may return to their experiment which has already been described and

* The table also indicates the percentage amount by which the potential difference, after various intervals, has approached the initial value.

criticised. They found that in about a week the spongy, lead gave off *forty-nine* times its volume of hydrogen gas and then it is stated that the spongy metal possesses not only the property of absorbing the gas, but also of giving it off again *in part*, so that forty-nine does not represent the total number of volumes absorbed.

Two different methods were employed. The first of these was simply a modification of Frankland's, and the result was practically identical with that which he obtained, although great precautions were taken to prevent the charged lead from coming into contact with the air, as thereby a portion of the absorbed hydrogen might be oxidised.

In the second method pure dry hydrogen (dried by means of phosphorus pentoxide), was led through melted lead contained in a U-tube. After the gas had passed through for 6 to 8 hours, the lead was allowed to cool down nearly to its melting-point, and the excess of hydrogen in the apparatus replaced by pure dry nitrogen. The U-tube was then connected with a combustion-tube containing ignited copper oxide, the other end of which had chloride of calcium tubes attached to it for the purpose of collecting water. In an experiment of this kind, however, where at the best only excessively small quantities of water were formed, the chloride of calcium ought to have been replaced by phosphorus pentoxide, as the nitrogen and oxygen which were employed were dried with this substance, and it is a well-known fact that gases so dried can take up water from chloride of calcium, which almost always contains a certain amount of moisture. After the apparatus was properly arranged and tested, oxygen was passed through it and the lead heated again to a higher temperature. Had any hydrogen been occluded by the lead it would have been converted into water and collected in the chloride of calcium tubes, but practically none was obtained. Another experiment was therefore made, but with this difference, that the melted lead was allowed to solidify completely before the excess of hydrogen was swept out by the nitrogen. The authors found that—

	Grm. Water.		Grms. Lead.	
I.	0·0022	was obtained when	200	were employed.
II.	0·0003	„ „ „	39·94	„ „

It is perfectly evident from these numbers that the quantity of water obtained is far too small to form the basis of any conclusions as to the occlusion of hydrogen by lead, but Neumann and Streintz calculate from them that lead absorbs 0·15 and 0·11 times its volume of hydrogen respectively. Rather more than one-tenth of its volume forms a striking contrast with the numbers given in the former paper, and it appears to us that, instead of proving that lead absorbs large quantities of hydrogen, it shows that it absorbs very little or none at all. The quantity of water obtained in these experiments, too, is apt to be very considerably increased if the solidified lead mechanically encloses bubbles of hydrogen. But the reasoning adopted by Neumann and Streintz is as follows. It has been shown by Graham that palladium used as the cathode on electrolysing dilute sulphuric acid absorbs much more hydrogen than when simply heated in an atmosphere of that gas, and similarly, if it can be shown that melted lead absorbs a certain amount of hydrogen, then they consider themselves justified in assuming that lead, used as an electrode, will absorb very much more. It is needless to say, however, that this reasoning, which may or may not be perfectly correct, cannot be adduced as a proof of the assumption which was made in their former paper.

Leipzig, February 22, 1892.

The Volatility of Urea and its Crystallisation by Means of Sublimation in a Vacuum.—Leon Bourgeois.—The sublimation of urea begins at about 120° to 130°, and it deposits crystals on the cold parts of the containing vessel.—*Bull. Soc. Chim. de Paris*, No. 2, 1892.

ON THE

ASSAY OF ORES OF ANTIMONY.

By AD. CARNOT.

As antimony has recently met with novel applications, the working of its ores has become much more active than heretofore. It has been complained, not without cause, that the assay of its ores by the usual processes of the dry way gave results very inaccurate and fluctuating in the hands of different operators. I have ascertained that the losses, always exceeding 8 per cent rise frequently up to 20 and even beyond 30 per cent of the true quantity, especially in poor ores.

After having made some attempts to diminish the losses by the dry process, which are always considerable on account of the volatility of antimony, I have studied a different method, the results of which have been much more satisfactory, and which on this account it seemed useful to make known.

The method consists, in principle, in dissolving the antimony in hydrochloric acid, in precipitating it with tin and weighing it in the metallic state. I indicate the precautions to be taken for sulphuretted ores, for oxides, and for those containing iron or lead.

1. *Sulphuretted Ores.*—We take from 2 to 5 grms. of the ore, according to its supposed percentage, so that we may operate upon about 1 grm. of metallic antimony. We attack it in a small flask with from 50 to 60 c.c. of concentrated hydrochloric acid, heating in the sand-bath, but not up to ebullition, so as to avoid losses by projection.

When the action seems to make no further progress we decant the clear liquid through a filter, adding in its stead a new quantity of acid, and resume the heating in the same manner until the sulphide is entirely dissolved. The acid is renewed once again, adding 1 or 2 drops of nitric acid to complete the attack, heating to 100°, and then washing the insoluble gangue with acid diluted with water.

The liquids decanted through the same filter are mixed with an equal volume of water; a blade of tin is introduced and heated to 80° or 90°. The precipitation begins at once, and for 1 grm. of antimony it is completed at the end of about 90 minutes.

The precipitate is washed by decantation, replacing the liquid by dilute hydrochloric acid to remove salts of tin and others derived from the attack and the precipitation. The metal is brought upon a tared filter, washed for some moments with hot water, and lastly with a little alcohol. The metallic antimony is then dried at 100° and weighed upon the same filter. If the operation is thus conducted there is neither loss nor appreciable oxidation.

The percentage of antimony is thus determined accurately in a short time. In several experiments made with stibine mixed with quartz I found that the variations were ordinarily quite minimal, and at the most did not exceed 1 centigrm.,—that is 1-100th of the true percentage of the ores operated upon.

2. *Oxidised Ores.*—The oxides of antimony, often mixed with sulphides not as yet perfectly transformed by atmospheric agents, are sometimes attacked with great difficulty by concentrated hydrochloric acid. We are then exposed either to notable losses by volatilisation or to an incomplete solution of the antimony.

I thought that we might easily convert the oxides into attackable sulphides by heating them very gently in an atmosphere of hydrogen sulphide, according to the method which I formerly proposed for the production of metallic sulphides (*Comptes Rendus*, 1879, July 21).

The ore, in very fine powder, is put into a small flat-bottomed flask, in which the quantity of from 2 to 5 grms. forms a light layer permeable to gases. We cause an elbowed tube to descend almost down to the level of the ore, securing it in its place by means of a cork resting in

the neck of the flask. Through this tube there is passed a current of dry sulphuretted hydrogen. The flask is placed upon wire gauze at the height of 4 or 5 c.m. above the flame of a Bunsen burner with its rose so that the temperature may not exceed 300°, not producing any volatilisation of the antimony sulphide. The ore remains pulverulent, and is pervaded with hydrogen sulphide, which acts at once as a reducing agent and as a sulphuriser. The surface is renewed from time to time by shaking the flask. There is produced a little vapour of water and sulphur, which condense on the upper part of the sides. The conversion is complete in an hour. When cold the sulphide is attacked with concentrated hydrochloric acid in the same flask. The precipitation and weighing are then effected as in the former case.

Experience shows that the quantity of antimony remaining undissolved is quite insignificant.

Ores containing Iron or Lead.

It often happens that antimony ores contain iron, not only in the state of oxide or of pyrites, but also as ferrous sulphide combined with antimony sulphide, and soluble together in hydrochloric acid. Its presence, even in important quantity, does not interfere with or complicate the process. The presence of zinc, which is very rare in these ores, occasions no difficulty.

Lead, as sulphide or as oxide, is found in some varieties of antimony ores. It dissolves in hot concentrated hydrochloric acid; its chloride may partly crystallise out during the cooling of the liquid, but another portion is deposited on the sheet of tin and renders the weight of the antimony excessive.

We may easily detect the presence of lead in the precipitate, and even determine its quantity by converting it into sulphide by means of a solution of yellow sodium sulphide (prepared by boiling the monosulphide with flowers of sulphur). If we heat the metallic powder to 50° or 60° in the solution of polysulphide, the antimony is rapidly dissolved, and the residue of lead sulphide is washed, dried, and weighed. Eight-tenths of the weight of this sulphide represents the corresponding weight of the metallic lead, but as the lead generally undergoes oxidation during drying the quantity may be estimated practically at nine-tenths the weight of the lead sulphide. This is then the correction to be made.—*Comptes Rendus*, cxiv., p. 587.

THE DETERMINATION OF FLUORINE.

By AD. CARNOT.

FLUORINE enters into the composition of many natural substances, but we have often restricted ourselves to establishing its presence by qualitative experiments on account of the difficulties presented by its exact determination, especially in presence of silicates.

Many methods of determination have certainly been given by eminent analysts—Berzelius, H. Rose, Woehler, Fresenius; but in these methods accuracy has been obtained only by means of great complications or very minute precautions.

The method which I now propose, and which I have already applied to the analysis of a certain number of fluorine compounds capable of being attacked by concentrated sulphuric acid, has the advantage of being of easy execution, and of not being interfered with by the presence of carbonates or of organic substances; it can serve to show not merely the proportion of fluorine, but also that of silicon with satisfactory accuracy.

The process is founded, like several methods already known, on the disengagement of fluorine in the state of gaseous silicon fluoride; its novelty consists in the method of determining the volatile compound. In place of calculating it by the difference of two weighings Woehler, Fresenius), or according to the weight of the calcium fluoride obtained after a tedious separation of the silica (Berzelius, H. Rose, and recently H. Lasne). I receive the silicon fluoride in a rather concentrated solution of pure potassium fluoride, with which it forms a precipitate of potassium silicofluoride, the weight of which enables us to calculate the fluorine, and if needful, the silicon, $SiF_2+KF=KF.SiF_2$, or $F_4+2KF=K_2F_6$.

I indicate briefly the arrangement of the apparatus and the course of the operation.

The mixture of fluoride and silicate is acted upon by concentrated sulphuric acid in a small flask holding 150 c.c., to the bottom of which there is conveyed a slow current of air, or of carbonic acid, which has been perfectly dried by passing through bottles filled with sulphuric acid. The gaseous current is then conveyed by an elbow-tube to the bottom of a flask containing a little mercury and above it 20 c.c. of a solution of pure potassium fluoride (1 part in 10). Beyond this there is an aspirator arranged so as to regulate the current.

The extremity of the tube which enters the flask should be drawn out to a point and bent back, opening 2 or 3 m.m. below the surface of the mercury, so that it is not moistened by the aqueous solution.

The flask and the tube must have been perfectly dried either in the stove or after the apparatus has been connected by the action of the dry gas conjointly with that of heat, so as to avoid any decomposition of silicon fluoride by moisture. The elbow-tube carries an empty bulb intended to retain the traces of sulphuric acid which may be carried along by the current of gas. There must be added a tube filled with pumice saturated with dehydrated copper sulphate to arrest the vapours of hydrochloric acid, when the fluoric substance contains also chlorides (apatite, &c.), for these vapours reacting upon the potassium fluoride might liberate hydrofluoric acid, which would attack the sides of the flask and the surface of the mercury.

The quantity of material taken for analysis should be such that the quantity of fluorine does not exceed about 0·100 grm.; we take therefore 0·200 grm. of rich fluorides (fluor-spar, cryolite, &c.), and up to 2 grms. or upwards of substances poor in fluorine (natural phosphates, bones, &c.). We mix the substance intimately in an agate mortar with ignited quartz in very fine powder in such proportions that there may be at least 10 parts of silica to 1 part of fluorine. The quantity of silica must be still greater if the matter under examination contains less that 5 or 6 per cent of fluorine.

When the apparatus has been fitted up, tested by means of the aspirator, and well dried, the current of gas is stopped for a few moments, we introduce into the flask the mixture to be attacked, and pour in 40 c.c. of pure concentrated sulphuric acid; then the current of gas is allowed to resume and the flask is heated upon a plate of iron, under which a gas-burner is lighted. At the same distance from the burner we place a similar flask also containing 40 c.c. of sulphuric acid, into which plunges a thermometer which indicates in a sufficiently approximate manner the temperature at which the action takes place (Fresenius); we regulate the burner so as to reach a temperature close upon 160°, which must never be exceeded.

The small flask is shaken from time to time so as to liberate the bubbles of gas which form in the liquid or against the sides; they generally cease to be formed after 1½ or 2 hours, and we may soon after consider the attack as completed.

The potassium fluoride contains then a gelatinous precipitate of silicofluoride which is scarcely visible, and which would soon settle if the liquid were left in repose; but without waiting for this we detach the tubes which lead to the flask, decant the aqueous solution, wash the mercury and the flask with several successive portions of water, and collect the liquids, the total volume of which should not exceed 100 c.c.; we add an equal volume of alcohol of the strength of 90 per cent, we mix the whole, and allow it to deposit.

When the precipitate is properly collected together after having decanted off the supernatant liquid and replaced it with dilute alcohol, we collect the deposit upon a tared filter, and finish the washing with alcohol diluted with its own volume of water, making use of the filter pump until the liquid no longer occasions any turbidity in a solution of barium chloride. We dry at 100° until the weight is constant, and calculate the fluorine of the silicon fluoride. For $1KF,SiF_2$ we have $F_2=0{\cdot}3451$.

For the accuracy of the determination it is essential that the reagents employed should be free from fluorine. This is certainly the case with sulphuric acid if it has been heated to close upon its boiling-point. It is the same with ignited quartz. However, both may be tested once for all in a blank experiment. The potassium fluoride should be free from silicofluoride; it is necessary to ascertain this point by dissolving 2 grms. of the salt in 100 c.c. of water, and adding an equal volume of alcohol at 90 per cent. No deposit should be produced even if the liquid is allowed to remain at rest for 24 hours.

In the analysis of a fluoric silicate one and the same operation may serve for the determination of the fluorine and of the silicon, provided that the sides of the flask are not sensibly attacked. This result is obtained either when we operate upon a silicate poor in fluorine, or if we mix very intimately by trituration in an agate mortar the fluoric substance with a great excess of quartz finely levigated and of pure silica, which is ignited and weighed exactly. The silicon is then calculated in two portions. A small portion is found along with the fluorine in the precipitate of silicofluoride. For $1KF,SF_2$ we have $Si=0{\cdot}12714$; $SiO_2=0{\cdot}28154$.

The other portion is found in the state of silica in the residue of the action of sulphuric acid, and may be separated and determined by the ordinary methods. The weight of the silica added must of course be deducted from the weight obtained.—*Comptes Rendus*, cxiv., p. 750.

THE FRACTIONAL ANALYSIS OF SILICATES.*

By F. W. CLARKE.

(Concluded from p. 189).

In the case of talc, $Mg_3H_2Si_4O_{12}$, the foregoing principle finds ready application. For this mineral two constitutional formulæ have been proposed; one,—

$$Mg_3H_2(SiO_3)_4,$$

regards it as an acid metasilicate; the other,—

$$Mg<\begin{matrix}Si_2O_5—MgOH\\Si_2O_5—MgOH\end{matrix},$$

represents it as a basic salt of the acid $H_2Si_2O_5$. Now talc is practically unattacked by hydrochloric acid either wet or dry, and so a presumption is established in favour of the metasilicate formula. The group —Mg—OH is apparently not present. This view, fortunately, is maintained by other evidence, which also serves to illustrate another principle in fractional analysis.

When talc is sharply and quickly ignited, so as to produce complete dehydration, silica is set free. That silica may then be dissolved out by boiling with an aqueous solution of sodium carbonate, and estimated. One-fourth of the total silica of the mineral was thus liberated, its quantitative determination varying only 0·21 per cent from the exact amount required. This decomposition represents a splitting up of talc in accordance with the following equation:—

$$Mg_3H_2Si_4O_{12}=3MgSiO_3+SiO_2+H_2O,$$

which is reconcilable only with the metasilicate formula. If the pyrosilicate formula were correct, the expulsion of water would be indicated thus:—

$$Mg<\begin{matrix}Si_2O_5—MgOH\\Si_2O_5—MgOH\end{matrix}=Mg<\begin{matrix}Si_2O_5—Mg\\Si_2O_5—Mg\end{matrix}>O+H_2O,$$

and it is not easy to see how silica could be split off. In short, the separation of the silica into two fractions, and the evidence furnished by the stability of the talc towards acids, prove that the hydrogen of the mineral is acid hydrogen, and establish the constitution of the species. Of all the possible formulæ for talc, the metasilicate formula alone satisfies the experimental conditions.

It has already been stated that the silicates under discussion, with the exception of talc, are readily decomposable by aqueous hydrochloric acid. Upon ignition, however, most of them split up into soluble and insoluble portions, which can be separately investigated. Serpentine, for example, splits up into soluble olivine and insoluble enstatite, water, of course, being eliminated. This particular case of decomposition by heat has long been known, but among the chlorites and the clintonite micas are found some new applications of the principle. Four examples, closely related, may be cited here, namely, three chlorites of similar type, and xanthophyllite, variety walnewite, from Siberia.

The method of investigation was as follows:—Each mineral, of which a sample had been previously analysed, was strongly ignited in powder over a blast. The operation was performed in a covered platinum crucible, and the ignition lasted for several hours. The material was next digested with strong hydrochloric acid, the mixture was evaporated to dryness, the residue treated with weak acid, and finally filtered off. There remained in the filter, of course, the insoluble portions of the minerals, plus the silica which had been liberated from the soluble parts. This silica was then removed by boiling with sodium carbonate solution, and the undissolved remainder was washed, weighed, and separately analysed. In each of the four cases it proved to have the composition of spinel, $MgAl_2O_4$, and in quantity it bore a definite relation to the formulæ of the original minerals. The latter were as follows, with their empirical formulæ subjoined:—

a. Ripidolite (clinochlore), from West Chester, Pa.
b. Clinochlore, from Slatoust, Urals.
c. Leuchtenbergite, from Slatoust, Urals.
d. Walnewite, from near Slatoust.

a. $Al_{38}Mg_{86}H_{140}(SiO_4)_{50}O_{113}$.
b. $Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$.
c. $Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{121}$.
d. $Al_{86}Ca_{24}Mg_{52}H_{50}(SiO_4)_{28}O_{174}$.

Upon dehydration these become:—

a. $Al_{38}Mg_{86}(SiO_4)_{50}O_{43}$.
b. $Al_{38}Mg_{87}(SiO_4)_{52}O_{42}$.
c. $Al_{42}Mg_{86}(SiO_4)_{50}O_{49}$.
d. $Al_{86}Mg_{52}Ca_{24}(SiO_4)_{28}O_{149}$.

Here we have throughout an excess of oxygen over the group SiO_4, and to that excess the amount of spinel formed by ignition is almost quantitatively proportional.

That a decomposition of this sort furnishes strong evidence relative to the constitution of the minerals in question is clear without argument. Since, however, it is the purpose of the present paper merely to give a brief indication of methods in fractional analysis, an elaborate theoretical discussion would be out of place in it. The data, in all their relations, are being fully considered elsewhere (*Am. Journ. Sci.*, Oct., Nov., Dec., 1890; Sept., 1891; March, April, 1892), and only a short notice of their bearing is needed here. In the chlorites the group —Mg—OH is certainly present; and the three examples here given all reduce to the general formula $Mg_2(SiO_4)_2R'_4$, in which R′ is partly H, partly MgOH, and partly AlO_2H_2. The juxtaposition of the two latter groups serves to explain the formation of spinel upon ignition; while the soluble portions of the decomposed material appear to be mixtures of olivine and magnesian garnet, minerals which are common sources of chlorites in nature. Quite recently, Tschermak has sought to show that these particular chlorites are mixtures of amesite and serpentine. But serpentine, when ignited, yields insoluble enstatite,

* *Journal of the American Chemical Society*, xiii., No. 10.

while the three chlorites studied give only spinel in the residue undissolved by hydrochloric acid. The inference is that the chlorites contain no serpentine molecules, and Tschermak's view becomes untenable.

In the case of the walnewite, the spinel reaction has peculiar interest. In that mineral, the most basic known member of the clintonite group, there is good reason for assuming the existence of a univalent group—

$$Al\langle{}^{O}_{O}\rangle Mg, \text{ or } -Mg-O-Al=O,$$

each form of expression having its own theoretical advantages. The walnewite itself appears to be a mixture of isomorphous molecules, among which the compound $(AlO_2Mg)_4SiO_4$ is predominant. Such a compound might easily split up into olivine and spinel, $Mg_2SiO_4+2MgAl_2O_4$, and the quantity of spinel actually formed when walnewite is decomposed by heat is almost exactly the amount required by theory. Two of the groups $-AlO_2Mg$, coalesce, with removal of one atom of magnesium, to form spinel, while the magnesium thus eliminated goes into the soluble olivine. The fact that the clintonite micas are almost invariably associated with spinel in nature, and frequently also with members of the olivine group, is very suggestive in this connection. The evidence of natural association and the evidence from the laboratory converge to one set of conclusions.

In the light of the foregoing statements the term "fractional analysis" practically defines itself. It is really an attempt at rational, as distinguished from empirical analysis; and it brings into the mineralogical laboratory the methods of the organic chemist. As yet, little more than a beginning has been made, but the field is promising and should yield a rich crop of valuable data. The researches are still in progress, and the results will be made public as rapidly as may be possible.

ON THE RELATIVE DENSITIES OF HYDROGEN AND OXYGEN. II.*

By Lord RAYLEIGH, Sec.R.S.

In a preliminary notice upon this subject (*Roy. Soc. Proc.*, vol. xliii., p. 356, Feb., 1888), I explained the procedure by which I found as the ratio of densities 15·884. The hydrogen was prepared from zinc and sulphuric, or from zinc and hydrochloric, acid, and was liberated upon a platinum plate, the generator being, in fact, a Smee cell, enclosed in a vessel capable of sustaining a vacuum, and set in action by closing the electric circuit at an external contact. The hydrogen thus prepared was purified by corrosive sublimate and potash, and desiccated by passage through a long tube packed with phosphoric anhydride. The oxygen was from chlorate of potash, or from mixed chlorates of potash and soda.

In a subsequent paper on the "Composition of Water" (*Roy. Soc. Proc.*, vol. xlv., p. 425, Feb., 1889), I attacked the problem by a direct synthesis of water from weighed quantities of the two component gases. The ratio of atomic weights thus obtained was 15·89.

At the time when these researches were commenced, the latest work bearing upon the subject dated from 1845, and the number then accepted was 15·96. There was, however, nothing to show that the true ratio really deviated from the 16 : 1 of Prout's law, and the main object of my work was to ascertain whether or not such deviation existed. About the year 1888, however, a revival of interest in this question manifested itself, especially in the United States, and several results of importance have been published. Thus Professor Cooke and Mr. T. W. Richards found a number which, when corrected for an error of weighing that had at first been overlooked, became 15·869.

The substantial agreement of this number with those obtained by myself seemed at first to settle the question, but almost immediately afterwards there appeared an account of a research by Mr. Keiser, who used a method presenting some excellent features, and whose result was as high as 15·949. The discrepancy has not been fully explained, but subsequent numbers agree more nearly with the lower value. Thus Noyes obtains 15·896, and Dittmar and Henderson give 15·866.

I had intended further to elaborate and extend my observations on the synthesis of water from weighed quantities of oxygen and hydrogen, but the publication of Professor E. W. Morley's masterly researches upon the "Volumetric Composition of Water" (*Amer. Journ. Sci.*, March, 1891) led me to the conclusion that the best contribution that I could now make to the subject would be by the further determination of the relative densities of the two gases. The combination of this with the number 2·0002,* obtained by Morley as the mean of astonishingly concordant individual experiments, would give a better result for the atomic weights than any I could hope to obtain directly.

In all work of this sort the errors to be contended with may be classed as either systematic or casual. The latter are eliminated by repetition, and are usually of no importance in the final mean. It is systematic errors that are most to be dreaded. But although directly of but little account, casual errors greatly embarrass a research by rendering difficult and tedious the detection of systematic errors. Thus in the present case almost the only source of error that can prejudice the final result is impurity in the gases, especially in the hydrogen. The better the hydrogen, the lighter it will prove; but the discrimination is blunted by the inevitable errors of weighing. After perhaps a week's work it may become clear that the hydrogen is a little at fault, as happened in one case from penetration of nitrogen between the sealed-in platinum electrodes and the glass of the generator.

Another difficulty which affects the presentation of results turns upon the one-sided character of the errors most to be feared. As has been said, impure hydrogen can only be too heavy, and another important source of error, depending upon imperfect establishment of equilibrium of pressure between the contents of the globe and the external atmosphere, also works one-sidedly in the same direction. The latter source of error is most to be feared immediately after a re-greasing of the tap of the globe. The superfluous grease finds its way into the perforation of the plug, and partially blocks the passage, so that the six minutes usually allowed for the escape of the initial excess of pressure in the globe may become inadequate. Partly from this cause and partly from incomplete washing out of nitrogen from the generator, the first filling of a set was so often found abnormally heavy that it became a rule in all cases to reject it. From these and other causes, such as accidental leakages not discovered at the time, it was difficult to secure a set of determinations in which the mean really represented the most probable value. At the same time, any arbitrary rejection of individual results must be avoided as far as possible.

In the present work two objects have been especially kept in view. The first is simplicity upon the chemical side, and the second the use of materials in such a form that the elimination of impurities goes forward in the normal working of the process. When, as in the former determinations, the hydrogen is made from zinc, any im-

* From the *Proceedings of the Royal Society*, vol. l. Read Feb. 18, 1892

* It should not be overlooked that this number is difficult to reconcile with views generally held as to the applicability of Avogadro's law to very rare gases. From what we know of the behaviour of oxygen and hydrogen gases under compression, it seems improbable that volumes which are as 2·0002 : 1 under atmospheric conditions would remain as 2 : 1 upon indefinite expansion. According to the formula of Van der Waals, a greater change than this in the ratio of volumes is to be expected.

purity which that material may contain and communicate to the gas cannot be eliminated from the generator; for each experiment brings into play a fresh quantity of zinc, with its accompanying contamination. Moreover, the supply of acid that can be included in one charge of the generator is inadequate, and good results are only obtained as the charge is becoming exhausted. These difficulties are avoided when zinc is discarded. The only material consumed during the experiments is then the water, of which a large quantity can be included from the first. On the other hand, the hydrogen liberated is necessarily contaminated with oxygen, and this must be removed by copper contained in a red-hot tube. In the experiments to be described, the generator was charged with potash,* and the gases were liberated at platinum electrodes. In the case of a hydrogen filling the oxygen blew off on one side from a mercury seal, and on the other the hydrogen was conveyed through hot tubes containing copper. The bulk of the aqueous vapour was deposited in a small flask containing strong solution of potash, and the gas then passed over solid potash to a long tube packed with phosphoric anhydride. Of this only a very short length showed signs of being affected at the close of all operations.

With respect to impurities, other than oxygen and oxides of hydrogen, which may contaminate the gas, we

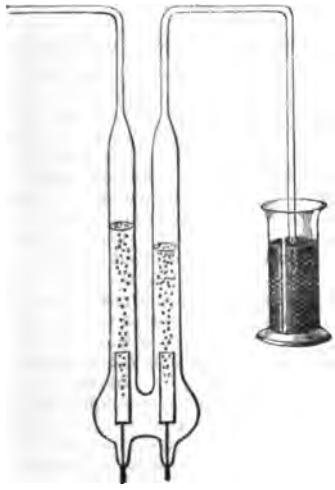


FIG. 1.

have the following alternative. Either the impurity is evolved much more rapidly than in proportion to the consumption of water in the generator, or it is not. If the rate of evolution of the impurity reckoned as a fraction of the quantity originally present, is not much more rapid than the correspondingly reckoned consumption of water, the presence of the impurity will be of little importance. If on the other hand, as is probable, the rate of evolution is much more rapid than the consumption of water, the impurity is soon eliminated from the residue, and the gas subsequently generated becomes practically pure. A similar argument holds good if the source of the impurity be in the copper, or even in the phosphoric anhydride; and it applies with increased force when at the close of one set of operations the generator is replenished by the mere addition of water. It is, however, here assumed that the apparatus itself is perfectly tight.

Except for the reversal of the electric current, the action of the apparatus is almost the same whether oxygen or hydrogen is to be collected. In the latter case the copper in the hot tubes is in the reduced, and in the former case in the oxidised, state. For the sake of distinctness we will suppose that the globe is to be filled with hydrogen.

The generator itself (Fig. 1) is of the U-form, with unusually long branches, and it is supplied from Grove cells with about 3 ampères of electric current. Since on one side the oxygen blows off into the air, the pressure in the generator is always nearly atmospheric. Some trouble has deen caused by leakage between the platinum electrodes and the glass. In the later experiments to be here recorded these joints were drowned with mercury. On leaving the generator the hydrogen traverses a red-hot tube of hard glass charged with copper,* then a flask containing a strong solution of potash, and afterwards a second similar hot tube. The additional tube was introduced with the idea that the action of the hot copper in promoting the union of the hydrogen with its oxygen contamination might be more complete after removal of the greater part of the oxygen, whether in the combined or in the uncombined state. From this point onward the gas was nearly dry. In the earlier experiments the junctions of the hard furnace tubes with the soft glass of the

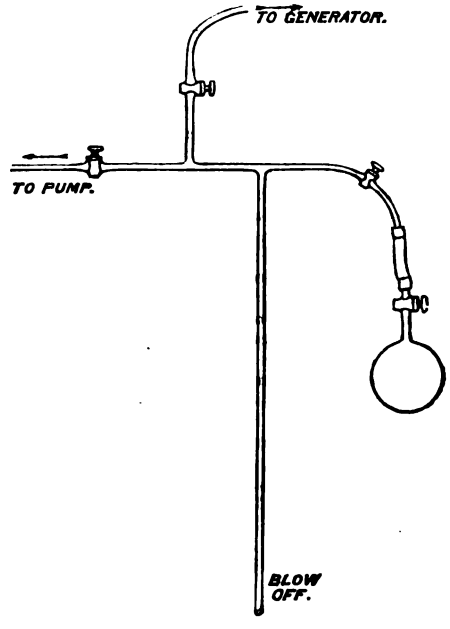


FIG. 2.

remainder of the apparatus were effected by fusion. One of these joints remained in use, but the others were replaced by indiarubber connections *drowned in mercury*. It is believed that no leakage occurred at these joints; but as an additional security a tap was provided between the generator and the furnace, and was kept closed whenever there was no forward current of hydrogen. In this way the liquid in the generator would be protected from any possible infiltration of nitrogen. Any that might find its way into the furnace tubes could easily be removed before the commencement of a filling.

Almost immediately upon leaving the furnace tubes the gas arrives at a tap which for distinctness may be called the regulator. In the generator and in the furnace tubes the pressure must be nearly atmospheric, but in the globe there is (at the commencement) a vacuum. The transition from the one pressure to the other takes place

* At the suggestion of Professor Morley, the solution was freed rom carbonate or nearly so, by the use of baryta, of which it contained a slight excess.

* The copper must be free from sulphur; otherwise the contamination with sulphuretted hydrogen is somewhat persistent.

at the regulator, which must be so adjusted that the flow through it is approximately equal to the production of gas. At first the manipulation of the regulator was a source of trouble and required almost constant attention, but a very simple addition gave the desired control. This was merely a long wooden arm, attached to the plug, which served both as a lever and as an indicator. Underneath the pointed extremity was a small table to which its motions could be referred. During the first two-thirds of a filling very little re-adjustment was needed, and the apparatus could be left for half an hour with but little fear of displacing too much the liquid in the generator. Towards the close, as the motive force fell off, the tap required to be opened more widely. Sometimes the recovery of the level could be more conveniently effected by insertion of resistance into the electric circuit, or by interrupting it altogether for a few minutes. Into details of this kind it is hardly necessary to go further.

From the regulator the gas passed to the desiccating tubes. The first of these was charged with fragments of solid potash, and the second with a long length of phosphoric anhydride. Finally, a tube stuffed with glass wool intercepted any suspended matter that might have been carried forward.

The connexion of the globe with the generator, with the Töppler, and with the blow-off, is shown in the accompanying Fig. 2. On the morning of a projected filling the vacuous globe would be connected with the free end of the stout-walled india-rubber tube, and secured by binding wire. The generator being cut off, a high vacuum would be made up to the tap of the globe. After a couple of hours' standing the leakage through the india-rubber and at the joints could be measured. The amount of the leakage found in the first two hours was usually negligible, considered as an addition to a globeful of hydrogen, and the leakage that would occur in the hours following would (in the absence of accidents) be still smaller. If the tests were satisfactory, the filling would proceed as follows:—

The electric current through the generator being established and the furnace being heated, any oxygen that might have percolated into the drying tubes had first to be washed out. In order to do this more effectively a moderate vacuum (of pressure equal to about 1 inch of mercury), was maintained in the tubes, and up to the regulator by the action of the pump. In this way the current of gas is made very rapid, and the half hour allowed must have been more than sufficient for the purpose. The generator was then temporarily cut off, and a high vacuum produced in the globe connexion and in the blow-off tube, which, being out of the main current of gas, might be supposed to harbour impurities. After this the pump would be cut off, the connexion with the generator re-established, and finally, the tap of the globe cautiously opened.

The operation of filling usually occupied from two to three hours. When the gas began to blow off under an excess of pressure represented by about half an inch of mercury, the blow-off cistern was lowered so as to leave the extremity of the tube free. For two minutes the current of gas from the generator was allowed to flow through, after which the generator was cut off, and the globe left in simple communication with the atmosphere, until it was supposed that equilibrium of pressure had been sufficiently established. Doubts have at various times been felt as to the interval required for this purpose. If too little time is allowed, there will remain an excess of pressure in the globe, and the calculated weight of the filling will come out too high. On the other hand, an undue prolongation of the time might lead to a diffusion of air back into the globe. In a special experiment no abnormal weight was detected after half an hour's communication, so that the danger on this side appeared to be small. When the passages through the taps were free from grease, one or two minutes sufficed for the establishment of equilibrium, but there was always a possibility of a partial obstruction. In the results to be presently given, four minutes were allowed after the separation from the generator. It may be remarked that a part of any minute error that may arise from this source will be eliminated in the comparison with oxygen, which was collected under like conditions.

The reading of the barometers and thermometers at the moment when the tap of the globe was turned off took place as described in the former paper. The arrangements for the weighings were also the same.

In the evacuations the process was always continued until, as tested by the gauge of the Töppler after at least a quarter of an hour's standing, the residue could be neglected. Here, again, any minute error would be eliminated in the comparison of the two gases.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 8th, 1892.

Dr. J. H. Gladstone, F.R.S., Past President, in the Chair.

Mr. C. S. Mitchell was elected a member of the Society.

Mr. Walter Baily, M.A., read a paper "*On the Construction of a Colour Map.*"

By the term "colour map," the author meant a diagram, each point of which defines by its position some particular colour. Captain Abney had shown that all colours except the purples could be formed by adding white light to some spectrum colour; whilst all except the greens could be made to produce white by the addition of some spectrum colour. There were therefore two ways in which colours, other than greens and purples, could be indicated. In one of these, the ordinate of a point might represent the spectrum colour by its wavelength and the abscissa, measured to the right of a vertical spectrum line, the amount of white light to be added to the spectrum colour to produce the colour represented by the point. In the other, the abscissa of a point situated on the left of the spectrum line represents the quantity of white light produced by the addition of the spectrum colour to the colour indicated by the point.

Regarding the spectrum colours as formed by mixing three primary colours (red, green, and violet) in varying proportions, three curves were drawn to the left of the spectrum line whose abscissæ represented respectively the proportions of the three primary colours present in the corresponding spectrum colour. Horizontal distances from any point to these curves show the proportions in which the primary colours are to be mixed to produce the particular colour defined by that point. For points between the curves, the horizontal distances are not measured all in one direction, and therefore indicate abnormal or imaginary colours.

The principle of the map was further illustrated by a sort of colour staff, consisting of three horizontal lines representing the three primary colour sensations (see Fig.)

of such luminosities that equal lengths of the three lines indicate white light. If points R, G, V, be taken in these lines, then a cross line, A, will cut off lengths A R, A G, A V, whose mixture will produce a certain colour. If, now, A be moved parallel to itself towards the right, the colour will change by the addition of white light; moving

A to the left means a subtraction of white light. When R, G, and V are properly chosen, a certain position, S, of the cross line corresponds to a spectrum colour. The whole of the series of colours which can be obtained by adding white light to that spectrum colour, can then be represented by sliding A towards the right. Positions S' and A' give colours complementary to S and A.

The distinguishing features of such a series of colours are the differences R−G and G−V, and the author calls the ratio $\frac{R-G}{G-V}$ the "*colour index*." Passing up the spectrum from red to violet, the index, which is first large and positive, diminishes and becomes negative between the yellow and blue; it then passes through infinity and becomes positive and decreases to zero.

The subject of determining the indices of colours resulting from the mixture in various proportions of two other colours whose indices were known was considered, and diagrams showing the various curves exhibited. Experimental methods of determining the proportions of the primary colour sensations constituting the spectrum tints were described.

A VISITOR enquired how the author's system provided for the class of colours outside the red and violet. He also desired a definition of "white light." He himself had never been able to produce pure white by mixture of colours, for a reddish violet generally resulted. On the other hand, he found it possible to match any other colour by mixture.

Prof. CAREY FOSTER thought Helmholtz was the first to propound the laws which the author had attributed to Captain Abney. He wished to know how the amounts of colour sensation were supposed to be measured. White light he considered ought to be defined as light in which a normal eye, not fatigued, could perceive no preponderance of any colour.

Mr. BLAKESLEY said that if white light was a mixture and only two unknowns were necessary, then any colour could be produced by the mixture of two other colours.

Dr. SUMPNER pointed out that white light was by no means a constant colour, but depended greatly on the source. He thought the author's map of a more absolute nature than that proposed by Maxwell.

Dr. HOFFERT enquired whether the intensities of each spectrum colour had been considered equal or otherwise taken into account, and also whether the results arrived at would be true for intensities other than those shown.

Mr. BAILY, in reply, said Captain Abney had found the light from the crater in the positive carbon of an electric arc to be the most constant white, and, in his method of experimenting, errors due to variation of the source cancel led. The quantity of any spectrum colour was defined by the breadth of the band used; the breadth being measured on the scale of wave-lengths.

A paper on "*A Mnemonic Table for Changing from Electrostatic to Practical and C.G.S. Units*" was read by Mr. W. GLEED, M.A.

In the table which is given below the abbreviations *Stat.* and *Mag.* are used to denote the electrostatic and electromagnetic units, and v stands for 3×10^{10}:—

To form the table, the numbers 9, 8, 1 in the middle of the second line give the value of "*g*." The end numbers are duplicated, giving 9, 9, 8, 1, 1. Below them, in the fourth line, come the names of the practical units, the initials forming the word "*fovac*." Remembering that the electromagnetic units of resistance and potential were too small for practical use, one places mag. above both ohm and volt. Ohm's law and definitions then show that the practical units of capacity, current, and quantity must be less than the electromagnetic unit; hence, mag. must be written below farad, ampère, and coulomb, since the practical units are intermediate in magnitude between stat. and mag., the vacant spaces are then filled in by stat. The v's in the bottom line are added in from memory. Several examples showing the use of the table are worked out in the paper accompanying the table.

A paper on "*The Law of Colour in Relation to Chemical Constitution*, by WILLIAM AKROYD, was read by Mr. BLAKESLEY.

The author has observed that in cases of compounds having a constant radical R and a variable radical R', the effect of an increase in the molecular weight of R' is to make the colour of the compound tend towards the red end of the colour scale. Exceptions are, however, noted.

Mr. H. M. ELDER questioned the author's conclusions, saying that in many cases the colours tend towards blue.

NOTICES OF BOOKS.

Saunders' Question Compounds, No. 23. *Essentials of Medical Electricity*. By D. D. STEWART, M.D., and E. S. LAWRANCE, M.D. Philadelphia: W. B. Saunders. 1892. Small 8vo., pp. 156.

WE cannot free ourselves from the suspicion that the work before us is what plain-spoken people do not scruple to call a "cram-book." But if so the information supplied should, at least, be accurate. Now, we read here (p. 25) that "metals are the best available conductors of electricity. Zinc, tin, and iron, named in their order of merit, head the list." If the authors had taken the trouble to consult some standard authority, *e.g.*, Ganot's "Physics," latest edition, they would have found that if we take the conductivity of silver at 100·0, and that of copper at 99·9, zinc has only 29·0, iron 16·8, and tin 13·1, so that they are much nearer the bottom than the head of the list.

We can scarcely accept the statement that electricity exists in three forms: Galvanic, Faradic, and Franklinic, or static electricity. Surely static electricity had been known and experimented upon before the days of Franklin. This, in fact, the authors admit in speaking of the experiments of Dr. Gilbert.

We notice a few errors which with a little more care might have been avoided. Thus the name of the illustrious Danish *savant* Oersted is in one place written "Oerstead." Leclanché figures here as Le Clanche. The words "intrauterine" and "extrauterine"—the latter especially—would read better if dissociated.

As regards the use of electricity in the treatment of disease we are unable to say whether the directions here laid would meet with the approval of leading medical authorities. It is high time, however, that medical electricity should be taken out of the hands of the charlatans by whom it is now exploited with equal audacity and success, using the last word merely of course in a pecuniary point of view.

On the Composition of Pinnaglobine.—a Novel Globuline.—Dr. A. B. Griffiths.—The substance in question is obtained from the blood of *Pinna squamosa*. Its composition is $C_{724}H_{985}N_{182}MnS_4O_{210}$. It does not combine with NO_2 or CO.—*Comptes Rendus*, vol. cxiv., No. 14.

Units of—	Capacity.	Resistance.	Potential.	Current.	Quantity.
Powers of 10 for practical and magnetic units	9	9	8	1	1
Small unit	Stat.	Mag.	Mag.	Stat.	Stat.
Practical unit	Farad.	Ohm.	Volt.	Ampère	Coulomb.
Large unit	Mag.	Stat.	Stat.	Mag.	Mag.
Factor for stat. and mag.	v^2	v^2	v	v	v

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bullatin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 2.

Certain Organic Haloid Derivatives.—C. Chabrié.—The author concludes that for 4 chlorine atoms of CCl_4 we may substitute the residues of 4 mols. of monosodium malonic ether (deprived of their atom of sodium). A new octobasic acid has thus been obtained. If we try to substitute the 4 residues of 4 mols. of sodium phenate (deprived of their atom of sodium) for the 4 atoms of chlorine of CCl_4 we cannot succeed, on account of the departure of the chlorine into an intermediate molecule,—a process promoted by the alkalinity of the medium. A synthesis of aurine has been effected in this manner. If organic haloid compounds are treated with silver fluoride in a sealed tube we obtain the corresponding fluorides. Methylene fluoride is antiseptic and not irritating. It destroys the bacillus of tuberculosis and the urinary pyrogenous bacterium. $C_2H_4Fl_2$ does not possess these properties, and we have examined how the number of the atoms of fluorine and the arrangement of the atoms in the molecule cause their physiological action to vary. The fluorides obtained are in general saponifiable by alcoholic potassa. The saponification of ethylene fluoride in the cold by means of lime produces a synthesis of glycol. The author has lastly shown the reciprocal substitutions occurring between boron and carbon in the haloid compounds and the oxides.

Method of Preparing Carvacrol.—A. Reychler.

Certain Derivatives of Carvacrol.—A. Reychler.

Constitution of Carvacrol.—A. Reychler.—For these three memoirs we must refer to the originals.

Series 3, Vols. vii. and viii., No. 3.

Action of Benzyl Chloride upon Non-Symmetric Metaxylidine.—M. Jablin-Gonnet.—The salts of methylbenzylmetaxylidine, such as the sulphate, the nitrate, and the hydrochlorate, are white and crystallise readily. Those of benzoylbenzylmetaxylidine, such as the sulphate, the hydrochlorate, and the oxalate, crystallise less readily and are white, with the exception of the nitrate, which is yellow.

Fixation of Atmospheric Nitrogen by the Soil and by Plants.—Arm. Gautier and R. Drouin.—The authors first give a history of this controverted question. They examine separately (A) the progress of the assimilation of nitrogen, first in a fertile soil, devoid of vegetation, and (1) deprived of organic matter and iron; (2) the same soil mixed with salts or iron oxide; (3) in the same soil mixed with organic matter; (4) in the same soil mixed at once with organic matter and ferric oxide. (B) in the same soils with or without iron or organic matter, but after seeds have been sown in them. For determining the nitrogen they reject the processes of Kjeldahl and of Will-Varrentrap and adopt a modification of the method of Schlœsing and Müntz. A tube of Bohemian glass of 1·20 metres in length and from 18 to 20 m.m. in internal diameter is sealed at its posterior extremity and slightly bent in the form of a gun-stock, which extends beyond the furnace grate by about 15 c.c. Into this tube they introduce (1) 18 grms. potassium chlorate melted and powdered and 6 grms. copper oxide (this mixture fills two-thirds of the bent part of the tube); (2) manganese carbonate for a length of about 10 c.m. intended to supply carbonic acid to sweep gases out of the tube at the beginning and at the end of the combustion; (3) cupric oxide in short tablets for the length of 12 c.m.; (4) 40 grms. of the soil to be analysed, not dried (its moisture having been determined in another specimen), carefully mixed in a bronze mortar with 180 grms. cupric oxide; (5) a long column of cupric oxide; (6) a good quantity of reduced copper, pulverulent and well broken up, extending for about 15 c.m. and filling the tube. Each of these portions is separated from the others by plugs of coarse fibres of asbestos, previously ignited. The tube is coated with copper foil from behind forwards, up to the column of reduced copper. It is placed in the furnace, and the air is expelled from it by repeatedly exhausting with a Gay-Lussac pump, liberating carbonic acid each time from the manganese carbonate, especially after the last stroke of the pump. The combustion is then effected in the ordinary manner. When all the part resting on the grate has been heated to redness, the potassium chlorate is moderately heated so as to liberate the oxygen until the reduced copper begins to be oxidised. This tube is then swept with a current of carbonic acid obtained by again heating the manganese carbonate. After the combustion the authors introduce into the gas receiver, placed over mercury and containing potassa-lye, a few c.c. of a concentrated solution of pyrogallol in case a trace of oxygen should have been introduced, and the volume of gas is then read off. The first series of experiments proves that the organic matter of the soil fix nitrogen independently of any vegetation. The second series shows that vegetation, especially leguminous plants, constitute a mode of the fixation of nitrogen. The authors are continuing their researches.

Synthetic Formation of Acetylene at the Expense of Bromoform.—P. Cazeneuve.—Already inserted.

The Chloroiodide of Certain Organic Bases.—A. Pictet and G. Krafft.—The authors describe the chloroiodides of pyridine, of quinoleine, piperidine, and trimethylamine.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Medical, 8.30.
TUESDAY, 26th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Sculpturing of Britain—its Later Stages," by Prof. T. G. Bonney, D.Sc., F.R.S.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Society of Arts, 8. "Australasia—its Progress and Resources," by Sir Edward Braddon, K.C.M.G.
WEDNESDAY, 27th.—Society of Arts, 8. "Egyptian Agriculture," by Prof. Robert Wallace.
—— Geological, 8.
THURSDAY, 28th.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
—— Society of Arts, 4.30. "Reorganisation of Agricultural Credit in India," by Sir William Wedderburn.
—— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.
FRIDAY, 29th.—Royal Institution, 9. "The Physiology of Dreams," by Dr. B. W. Richardson, F.R.S.
SATURDAY, 30th.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

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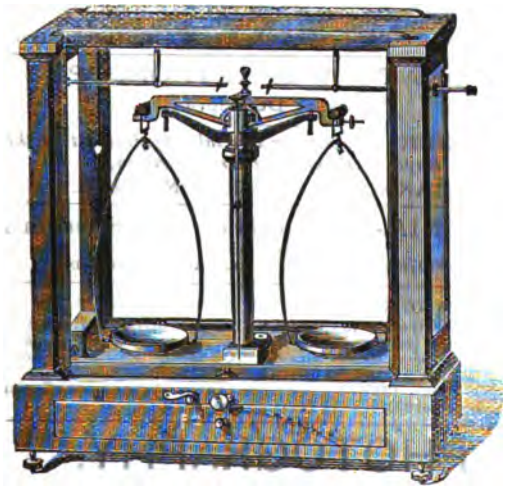

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RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

THE great interest which the rare earths claim in recent times render it desirable in the first place to submit to a more thorough study the imperfectly known metals of the cerium group, and especially the complex of elements hitherto comprised under the name of didymium. As the older methods for separating the cerite metals are for the most part very tedious, and as the methods published by Auer von Welsbach have been found in many respects far preferable, though in part dependent on certain conditions which the author has not always laid down with sufficient precision, I purpose considering some of the conditions which are required for the success of the different processes. On the theory of the latter only few indications can be given, as the explanation of several of the reactions which come into play must be reserved for future investigations.

As primary material there served a *cerium oxalicum purissimum* and a *cerium carbonicum purissimum* obtained in commerce, and alleged to have been obtained from oxalate and carbonate prepared from Norwegian orthite, from which a portion of the cerium had already been separated.

1.—*Preparation of Pure Cerium Compounds, free from Lanthanum and Didymium.*

According to Auer von Welsbach (*Monats'hefte fur Chemie*, 1884 and 1885, p. 508), the preparation is best founded upon the ready crystallisability of ammonium-ceric nitrate, and the inability of the other rare earths (with the exception of thorium) to form salts of the stage of oxidation corresponding to cerium dioxide. The attempt must therefore be made to prepare in the simplest manner a solution of the earths in nitric acid containing all the cerium present or the greatest possible proportion of it as a salt of the dioxide. The earthy oxalates dried at 100° dissolve very readily on digestion in heat with an excess of nitric acid of specific gravity 1·40. Vapours of hyponitric acid are given off and there remain nitrates. Still the cerium would be present only as cerous salt; this would be the simplest method if a suitable oxidising agent could be found which would convert the cerium of this solution into ceric nitrate. Possibly hydrogen peroxide or lead peroxide might be available. In default of such an oxidising agent the oxalates must be converted into oxides by strong ignition in presence of air.

Pure cerium oxalate, as, indeed, all pure cerium salts with an organic acid, pass on ignition in the air very readily into cerium dioxide, which is unchangeable at all temperatures and is quite insoluble in nitric acid, whether concentrated or dilute. But if the solution from which the oxalate was precipitated contained lanthanum and didymium along with cerium, the oxide obtained is the more soluble in nitric acid the larger the proportion of the two latter metals. In the solution there is, along with cerium dioxide, always a considerable proportion of cerous oxide, whether the latter is already contained as such in the mixture of oxides or whether it is formed from the cerium dioxide with loss of oxygen. The solubility of the oxide in nitric acid depends not alone on the quantity of lanthanum and didymium present, but to a great extent on its mechanical condition, and on the presence of foreign impurities such as silica, ferric oxide, alkaline salts, &c. If the proportion of cerium oxides in the mixture exceeds 50 per cent, and but little of the impurities above mentioned are present, it may often be brought into solution by covering the dry oxide in a state of fine division at once with 4 parts of nitric acid (containing 50 per cent HNO_3). There ensues a copious escape of oxygen and a violent reaction, the mixture becoming heated to ebullition, and in a few seconds everything is dissolved to a dark reddish yellow liquid. If, on the other hand, the oxide is moistened with water and then digested at 100° with strong nitric acid, the reaction is very tedious, and even after digestion with the constant addition of fresh portions of acid, it is not practicable to dissolve all the oxide, doubtless because there are formed basic salts in the latter case, but not in the former.

A mixture of oxides as it is obtained by working up most cerite minerals, *e.g.*, cerite, is generally too rich in cerium to be dissolved in nitric acid as above mentioned. Hence it is necessary firstly to eliminate the larger portion of the cerium, according to one of the old methods, *e.g.*,

* *Berichte der Deutsch. Chem. Gesell.*

that of Debray (*Comptes Rendus*, xcvi., p. 828), fusing the nitrates with potassium nitrate, and we may proceed as follows:—

The oxide is ground up in a mortar with 1½ times its own weight of concentrated sulphuric acid; the mixture is transferred to a platinum capsule and heated gently whilst stirring until the mass has become yellow throughout and is converted into sulphate. When cold it is dissolved in a minimum of water without the application of heat; the liquid is allowed to deposit and the clear yellow solution is decanted off from the sediment.

It is then poured into a large excess of soda-lye, which has been previously heated in a porcelain capsule; the liquid is boiled for some time; the mixture of hydroxides, which consists chiefly of cerium hydroxide, is repeatedly washed by decantation with boiling water in the capsule, then poured into a large glass, and washed with cold water by decantation until no trace of sulphuric acid can be detected in the washings by means of hydrochloric acid and barium chloride. The precipitate is then filtered off and dried at 100°. It is now readily soluble in nitric acid of specific gravity 1·40.

As it is advantageous to combine the preparation of a pure cerium salt with that of lanthanum and didymium salts free from cerium, it is preferable not to dissolve the mixed oxides in which the latter metals have been caused to accumulate directly in nitric acid, but to use for this purpose the basic cerium precipitate to be described below.

In presence of foreign impurities which may be derived from the minerals used or the reagents applied (lead from sulphuric acid, silica from the soda-lye, &c.), it is advisable not to evaporate at once the nitric solution of the basic cerium precipitate or of the hydroxide (prepared as directed) with an addition of ammonium nitrate until it crystallises, but to allow it to stand in the first place in the cold for 12 hours, when the nitrates of lead, copper, &c., which are sparingly soluble in strong nitric acid, separate out. The clear liquid is then decanted off, the necessary quantity of ammonium nitrate is added (when the oxide or its corresponding quantity of hydroxide is worked up three-quarters of the weight of the latter), and in presence of silica the liquid is evaporated to dryness. The liberated silica after dissolving the saline residue in dilute nitric acid is then removed by filtration through asbestos. Filtration through paper, which is practicable if the liquid is sufficiently diluted, must be avoided on account of its reductive action.

In working up the basic cerium precipitate, the separation of any silicate present is generally not needful. We dissolve 100 parts of the precipitate nearly completely, dried at 100°, in 265 parts of nitric acid of specific gravity 1·40; any lead nitrate present is allowed to crystallise out; 113 parts of water and 39 parts of ammonium nitrate are then added as a saturated solution at a temperature close upon ebullition, and the liquid is evaporated down upon the water-bath until crystals begin to form upon the surface of the blackish liquid. It is then allowed to cool slowly and is set aside for twelve hours.

The chief part of the ceric salt present in the solution is thus obtained in small, shining crystals of the colour of potassium pyrochromate, and the composition—

$$Ce(NO_3)_4.2NH_4.NO_3,$$

which are agglomerated in tufts and crusts of little consistence. After further evaporating the reddish-yellow mother-liquor we obtain in the first place some more crystals of the same salt. Subsequently there crystallises out an isomorphous mixture of the double ammonium cerium (cerous) lanthanum and didymium nitrates in large crystals generally compactly coalescent, and having a light yellow colour from inclosed mother-liquor. The crystals have the composition $\overset{III}{R}(NO_3)_3.2NH_4NO_3.4H_2O$. They may easily be separated from the crystals of the ceric salt, and along with the mother-liquor they may be submitted anew to a process of separation by precipitation with oxalic acid, conversion into oxides, &c.

The ammonium-ceric nitrate is drained on a funnel with a cone of platinum wire gauze and dried upon unglazed porcelain under a bell-glass over quicklime and sodium hydroxide. For re-crystallising the salt it is best to use pure nitric acid free from chlorine and containing 40 per cent of HNO_3; 100 parts of the dried crystals are dissolved in a minimum of this acid, about 165 parts (99 parts nitric acid of specific gravity 1·40 and 66 parts of water) in a flask on the water-bath. The liquid is poured into a deep basin and evaporated until crystals appear. Re-crystallisation repeated three or four times is generally sufficient to remove from the salt the last traces of lanthanum and didymium. In this manner about 1400 grms. absolutely pure cerium double salt were obtained from the above material.

2.—*Obtaining Salts of Lanthanum and Didymium free from Cerium.*

If, as directed by Auer von Welsbach, we treat with moderately dilute nitric acid the finely-divided mixture of oxides of the cerite metals (obtained by precipitating with oxalic acid and igniting the oxalates), most of the lanthanum and didymium dissolve as nitrates, and if the proportions are properly selected and the reaction is sufficiently prolonged, all the cerium, to the last trace, passes into the precipitate absolutely insoluble in the liquid and consisting chiefly of basic nitrates. These assertions I can fully confirm, though if the mixture of oxides is very rich in cerium the reaction is very tedious and sometimes it does not take place, when again the presence of foreign impurities and other causes not easily ascertained play a part not unimportant. It is here advisable (as intimated in the former section) first to accumulate the lanthanum and didymium in the material operated upon and then proceed to the complete elimination of the cerium.

When by one or other method a solution has been obtained in which the proportion of the lanthanum and didymium oxides forms 50 per cent or more of the total earths, the separation of the earths is effected without difficulty if the following directions are accurately followed.

(To be continued).

ON THE RELATIVE DENSITIES OF HYDROGEN AND OXYGEN. II.*

By Lord RAYLEIGH, Sec.R.S.

(Concluded from p. 202).

IN the case of oxygen, the errors due to contamination (even with hydrogen) are very much diminished, and similar errors of weighing tell very much less upon the proportional agreement of the final numbers. A comparison of the actual results with the two kinds of gas does not, however, show so great an advantage on the side of the oxygen as might have been expected. The inference appears to be that the individual results are somewhat largely affected by temperature errors. Two thermometers were, indeed, used (on opposite sides) within the wooden box by which the globe is surrounded, and they could easily be read to within 1·20° C. But in other respects the circumstances were unfavourable in consequence of the presence in the same room of the furnace necessary to heat the copper. An error of ±0·1° C. in the temperature leads to a discrepancy of 1 part in 1500 in the final numbers. Some further elaboration of the screening arrangements actually employed would have been an improvement, but inasmuch as the circum-

* From the *Proceedings of the Royal Society*, vol. l. Read Feb. 18, 1892

stances were precisely the same for the two gases, no systematic error can here arise. The thermometers were, of course, the same in the two cases.

The experiments are grouped in five sets, two for oxygen and three for hydrogen. In each set the work was usually continued until the tap of the globe required regreasing, or until, owing to a breakage or to some other accident, operations had to be suspended.

Oxygen.

1891.	Weight. Grm.	Bar. temp., ° F.	Globe temp., ° C.
June 29	2·5182	70	20·85
July 2..	2·5173	69	20 60
,, 4..	2·5172	67½	19·75
,, 6..	2·5193	70½	21·40
,, 9..	2·5174	64	17·60
,, 10..	2·5177	65½	19·05
Mean	2·51785	68	20

The six fillings were all independent, except that of July 6, when the bulk of the oxygen remaining from the previous filling was not removed. It so happens that this case shows the greatest discrepancy, but there seems to be no sufficient reason for rejecting it.

Hydrogen.

1891.	Weight. Grm.	Bar. temp., ° F.	Globe temp., ° C.
July 31	0·15807	60½	15·90
August 4	0·15816	65	18·00
,, 6	0·15811	66½	19·20
,, 8	0·15803	65	18·15
,, 11	0·15801	66	19·15
,, 13	0·15809	68½	20·10
Mean	0·15808	65	18

Hydrogen.

1891.	Weight. Grm.	Bar. temp., ° F.	Globe temp., ° C.
September 22	0·15800	58	14·5
,, 24	0·15820	61½	16·3
,, 28	0·15792	62	17·6
,, 30	0·15788	63½	18·1
October 2	0·15783	62	17·3
Mean	0·15797	61	17

Hydrogen.

1891.	Weight. Grm.	Bar. temp., ° F.	Globe temp., ° C.
October 26	0·15807	55	13·30
,, 28	0·15801	56	14·00
,, 31	0·15817	50	10·95
November 3	0·15790	53½	12·10
,, 5	0·15810	55	12·00
,, 7	0·15798	50	10·70
,, 10	0·15802	48	9·30
,, 13	0·15807	55½	12·70
Mean	0·15804	53	12

Oxygen.

1891.	Weight. Grms.	Bar. temp., ° F.	Globe temp., ° C.
November 31	2·5183	53	12·15
December 3	2·5168	56	13·55
,, 5	2·5172	56½	14·15
,, 7	2·5181	58½	14·70
,, 8	2·5156	51	11·15
Mean	2·5172	55	13

In almost every case the weight of the globe *full* is compared with the mean of the immediately preceding and following weights *empty*. The numbers recorded in the second column are derived from the readings of the balance by the introduction of corrections—

(1) For the errors of the weights themselves, found by a systematic comparison, only relative values uncorrected for buoyancy being required.

(2) For the deviation of the mean (there were two barometers) barometric reading at the time of filling from 30 inches (as read upon the vernier).

(3) For the deviation of the temperature of the barometers (column 3) from 60° F.

(4) For the deviation of the temperature of the gas (as read upon the thermometers) from 12° C.

As an example I will take in detail the calculation for the hydrogen filling of October 26. After the evacuation of October 24, the working globe (14) with its compensating volume piece and 0·4778 grm. stood on the left of the balance with globe (11) on the right. The position of equilibrium of the pointer, as determined after four different releasements, each observed in the usual manner, was 19·02 scale divisions. In like manner, after the evacuation of October 27, with the same weights in use, the equilibrium position of the pointer was 18·46. After the filling of October 26, the weights associated with (14) were 0·3220 grm., instead of 0·4778; and the pointer reading was 20·08. So far as the weights are concerned, the value of the hydrogen would be 0·4778−0·3220, or 0·1558 grm.; but to this we must add a correction corresponding to 1·34 scale divisions, being the difference between 20·08 and ½(19·02+18·46). At the time in question, the value of a scale division was 0·00020 grm., so that we obtain—

$$0·1558+0·00027=0·15607.$$

The particular weights in use on this occasion were such that no correction is necessary in order to allow for their errors.

The mean barometer reading at the time of filling was 29·742, so that the factor required on this account is 30 : 29·742. The correction for temperature of gas is from 13·3 to 12°.

Log 0·15607	=1·19332
For barometer.. ..	0·00375
,, temperature ..	0·00198
Log 0·15814	=1·19905

To this a correction for the temperature of the *barometer* has still to be applied. For 1° F. the correcting factor is (1−0·000089), or for 5° F. (1−0·000445). From 0·15814 we are thus to subtract 0·00007, giving the tabular number 0·15807.

A further minute correction to the mean of each set may be made for the temperature of the glass. A warm globe is larger than a cold one, and consequently holds more gas. If we suppose that the volume expansion of the glass per degree C. is 0·000025, we find, corrected to 12° C.—

Hydrogen.

1891	Weight. Grm.	Bar. temp., ° F.	Globe temp., ° C.	Corrected to 12°. Grm.
July	0·15808	65	18	0·158056
September ..	0·15797	61	17	0·157950
October	0·15804	53	12	0·158040
Mean ..	—	60	16	0·158015

Oxygen.

1891.	Weight. Grms.	Bar. temp., ° F.	Globe temp., ° C.	Corrected to 12°. Grms.
June	2·51785	68	20	2·51735
November ..	2·51720	55	13	2·51713
Mean ..	—	61½	16½	2·57124

The means here exhibited give the weights of the two gases as they would be found with the globe ar 12° C., and the barometers at 60° F. and at 30 inches. The close agreement of the mean temperatures for the two gases shows how little room there is for systematic error dependent upon imperfections in the barometers and thermometers. But the results still require modification before they can be compared with the view of deducing the relative densities of the gases.

In the first place there is a systematic, though minute, difference in the pressures hitherto considered as corresponding. The terminal of the blow-off tube is 33 inches below the centre of the globe at the time of filling. In the one case this is occupied by hydrogen, and in the other by oxygen. If we treat the latter as the standard, we must regard the hydrogen fillings as taking place under an excess of pressure equal to $\frac{1}{16}$ of the weight of a column of oxygen 33 inches high; and this must be compared with 30 inches of mercury. Hence, if we take the sp. gr. of oxygen under atmospheric conditions at 0·0014, and that of mercury at 13·6, the excess of pressure under which the hydrogen was collected is as a fraction of the whole pressure—

$$\frac{33}{30} \cdot \frac{15}{16} \cdot \frac{0{\cdot}0014}{13{\cdot}6} = 0{\cdot}000106;$$

and 0·000106 × 0·158 = 0·000017. This, then, is what we must subtract from the weight of the hydrogen on account of the difference of pressures due to the gas in the blow-off tube. Thus—

$$H = 0{\cdot}157998, \qquad O = 2{\cdot}51724.$$

(These numbers are not quite comparable with those given in the former communication, inasmuch as the standard temperature then used *for the barometers* was 55° F. Reduced so as to correspond to 60°, the former numbers become—

$$H = 0{\cdot}15797, \qquad O = 2{\cdot}5174.$$

The agreement is satisfactory, especially when it is remembered that both gases were prepared by different methods in the two sets of experiments.—Feb. 17.)

But there is still another and a more important correction to be introduced. In my former paper it was shown that when the weighings are conducted in air the true weight of the gas contained in the globe is not given by merely subtracting the weight of the globe when empty from the weight when full. When the globe is empty, its external volume is less than when full, and thus, in order to obtain the true weight, the apparent weight of the gas must be increased by the weight of air whose volume is equal to the change of volume of the globe.

In order to determine the amount of this change of volume, the globe is filled to the neck with recently boiled distilled water, and the effect is observed upon the level in the stem due to a suction of, say, 20 inches of mercury. It is not advisable to carry the exhaustion much further for fear of approaching too nearly the point at which bubbles of vapour may be formed internally. In the earlier experiments, described in the preliminary note, the upper surface of the liquid was in the stem of the globe itself (below the tap), and the only difficulty lay in the accurate estimation of a change of volume occurring in a wide and somewhat irregular tube. The method employed was to produce, by introduction of a weighed quantity of mercury, a rise of level equal to that caused by the suction.

The advantage of this procedure lay in the avoidance of joints and of the tap itself, but, for the reasons given, the readings were not quite so accurate as might be desired. I wished, therefore, to supplement, if possible, the former determination by one in which the change of volume occurred in a tube narrower and of better shape. With this object in view, the stem of the globe was prolonged by a graduated tubular pipette attached with the aid of indiarubber. The tubes themselves were treated with gutta-percha cement, and brought almost into contact. It had hardly been expected that the joint would prove unyielding under the applied suction, but it was considered that the amount of the yielding could be estimated and allowed for by operations conducted *with tap closed*. The event, however, proved that the yielding at the joint was scarcely, if at all, perceptible.

The pipette, of bore such that 16 c.m. corresponded to 1 c.c., was graduated to 0·01, and was read by estimation to 0·001 c.c. In order the better to eliminate the changes due to temperature, readings under atmospheric pressure and under a suction of 20 inches of mercury were alternated. On January 28, 1892, a first set gave 0·648 − 0·300 = 0·348, a second gave 0·6645 − 0·316 = 0·3485, and a third gave 0·657 − 0·326 = 0·349. Similar operations with tap closed* gave no visible movement.

The result of the day's experiments was thus 0·3485 for 20 inches, or 0·523 for 30 inches, suction. Similar experiments on January 28, at a different part of the graduation, gave 0·526. On this day the yielding with tap closed was just visible, and was estimated at 0·001. As a mean result we may adopt 0·524 c.c. The graduation of the pipette was subsequently verified by weighing a thread of mercury that occupied a measured length.

A part of the above-mentioned volume is due to the expansion of the water when the pressure is relieved. We may take this at 0·000047 of the volume per atmosphere. The volume itself may be derived with sufficient accuracy for the present purpose from the weight of its oxygen contents. It is 2·517/0·00137, or 1837 c.c. The expansion of the water per atmosphere is thus 0·000047 × 1837, or 0·087 c.c. This is to be subtracted from 0·524, and leaves 0·437 c.c. This number applies strictly to the volume enclosed within the glass, but the change in the external volume of the globe will be almost the same.†

The correction now under consideration is, thus the weight of 0·437 c.c. of air at the average temperature of the balance room. The density of this air may be estimated at 0·00122, so that the weight of 0·437 c.c. is 0·000533 grm. This is the quantity which must be added to the apparent weights of the gases. The former estimate was 0·00056 grm. The finally corrected weights are thus—

$$H = 0{\cdot}158531, \qquad O = 2{\cdot}51777;$$

and for the ratio of densities we have—

$$15{\cdot}882.$$

This corresponds to a mean atmospheric condition of pressure and temperature.

If we combine the above ratio of densities with Prof. Morley's ratio of volumes, viz., 2·0002 : 1, we get, as the ratio of atomic weights, 15·880.

If we refer to the table we see that the agreement of the first and third series of hydrogen weighings is very good, but that the mean from the second series is decidedly lighter. This may have been in part fortuitous, but it is scarcely probable that it was so altogether. Under the circumstances we can hardly reckon the accuracy of the final results as closer than $\frac{1}{5000}$.

A word should perhaps be said upon a possible source of systematic error, viz., mercury vapour. There is no doubt that hydrogen passed over mercury takes up enough to cause a slow and superficial, but quite distinct, discolouration of sulphur, over which it subsequently flows. In the experiments here recorded, the gas did not, indeed, flow over mercury in mass, but, inasmuch as mercury was

* For greater security the tap was turned while the interior was under suction.

† For a spherical shell of glass of uniform thickness and with elastic constants following Poisson's law, the ratio of the difference of the internal and external expansion to either of them is $4t/3a$, where t is the thickness of the shell and a the mean radius. In the present application the value of $\frac{t}{a}$, deduced from the measured circumference and from the weight of glass, is about $\frac{1}{120}$.

(Perhaps an arrangement in which the *external* volume is directly measured would have been preferable. No allowance for expansion of water would then be needed.—Feb. 17).

used to secure the tightness of some of the joints, it is difficult to feel sure of its absence. Again, in evacuations conducted with a mercury pump, can the vacuum be regarded as free from mercury vapour, which, it must be remembered, would not show itself upon the guage of the Töppler? If both the hydrogen and the "vacuum" were saturated with mercury vapour, the result of the weighings would, according to Dalton's law, be free from its influence. The same may be said of any volatile impurity arising from the grease* upon the stop-cocks. As the matter stands, the results must, I think, be regarded as affected with a possible error amounting to a fraction of the weight of mercury vapour at the temperatures employed. But this is probably a very small quantity.

According to Hertz,† the vapour pressure of mercury at 15° C. would be about 0·001 m.m. If this be correct, the weight of mercury vapour in an atmosphere of hydrogen would be as a fraction of the latter—

$$\frac{0{\cdot}001}{760} \times 200 = \frac{1}{3800}.$$

It appears that in an investigation of hydrogen aiming at an accuracy of 1/10,000, the question of mercury vapour requires very careful consideration.

The accompanying table of results found by various experimenters may be useful for comparison:—

Name.	Date.	Atomic weights	Densities.
Dumas	1842	15·96	—
Regnault	1845	—	15·96
Rayleigh	1888	—	15·884
Cooke and Richards ..	1888	15·869	—
Keiser	1888	15·949	—
Rayleigh	1889	15·89	—
Noyes	1890	15·896	—
Dittmar	1890	15·866	—
Morley	1891	15·879	—
Leduc	1891	—	15·905
Rayleigh	1892	—	15·882

In conclusion, I must express my obligations to Mr. Gordon, who has assisted me throughout. The work has been unusually tedious, partly from its inherent nature, requiring as it does a certainty of 0·1 m.grm. in the weighings, and still more from the constant liability to accidents, which may render nugatory a large amount of preparatory work.

DIFFERENCES IN THE DETERMINATION OF REVERTED PHOSPHORIC ACID BY THE OFFICIAL METHOD OF ANALYSIS.‡

By CHARLES GIBSON.

Having found it utterly impossible to make my analyses for the amounts of reverted phosphoric acid in several consignments of high-grade aluminic phosphate agree within several per cent with those of Messrs. Stillwell and Gladding, of New York, both of us using the official method, I proceeded to investigate by numerous experiments. The conclusions I have arrived at, and the reasons therefor, together with a few of the results I and others have obtained, I now propose to lay before this Association.

When this material was first placed on the market my company, thinking perhaps we could use it profitably and advantageously in other respects in our factory, purchased a few consignments; and at the suggestion of the vendors we readily agreed to settle on the analyses of Messrs. Stillwell and Gladding, who were chemists of great eminence; and the fact of their using the official method of analysis contributed in no small degree to our ready assent. Their analyses of the different consignments, which they have since informed me were by the official method strictly as to time, temperature, &c., were checked by me, not using the official method, however, but using the method which I use in controlling the work in the factory—the alkaline citrate method of Joulie—our results invariably agreeing to within one-tenth of 1 per cent. Goods were in due time made up with this material as one of the ingredients, and samples drawn and submitted to the chemists of the various States where they were likely to be sold. On the reports from the State chemists coming to hand we were surprised to find that they all, without a single exception, gave a very much lower percentage of available P_2O_5 than we had a right to expect, amounting to about 15 per cent on the ton of aluminic phosphate used.

Investigation proved that there had been no mistake in the weighing out of the materials. The proportions were found to be correct, and nothing of a retrograde nature could be discovered, at least with the Joulie method of analysis. But, in using the official method on the prepared goods, I obtained results which agreed completely with those of the State chemists. Evidently there was something wrong somewhere, and an analysis of a sample drawn from one of the consignments of aluminic phosphate (using the official method, instead of the alkaline method) indicated in which direction the trouble lay. This analysis gave results of about 15 per cent available P_2O_5 less than had been found by Messrs. Stillwell and Gladding. Repeated analyses with the same and other solutions failed to change this, and an examination by the official method showed the same state of things with regard to every consignment we had received. Through the kindness of two of the State chemists, the Hon. M. A. Scovell, of Kentucky, president of this association, and Professor H. A. Huston, of Indiana, I have been able to verify the correctness of my results, at least as far as one consignment is concerned, as the following will show:—

Stillwell and Gladding found 34·73 per cent available P_2O_5; total P_2O_5, 47·04 per cent.

Mr. Scovell, 20·31 per cent available P_2O_5; total P_2O_5, 44·25 per cent.

Professor Huston, 19·40 per cent available P_2O_5; total P_2O_5, 45·46 per cent.

My own, by official method, 19·70 per cent available P_2O_5; total P_2O_5, 46·7 per cent.

My own, by alkaline method, 34·74 per cent available P_2O_5; total P_2O_5, 47·0 per cent.

This matter thus assumed for us a serious aspect, for here we were both buying and selling on analytical results obtained by the official method, and yet, from a cause over which we had not the slightest control, we were subjected to a financial loss of very serious proportions, amounting to between 10 dollars and 12 dollars per ton of aluminic phosphate used.

Continuing the investigation with a view of finding whether or not this serious evil could be avoided, I found that infinitesimal variations in the preparation of the ammonia citrate solution of the official method very materially changed the results in the determinations of reverted P_2O_5 in this material. Although in the preparation and use of the ammonia citrate solution the directions as laid down in *Bulletin* No. 24, page 224, were followed with the utmost care, I was totally unable to prepare two solutions that would give anything like concordant results; and even with the same solution they were anything but uniform. The cause of this I found to be owing to very slight unavoidable variations in the composition of the ammonia citrate solution. I also found that the slightest inclination to acidity very largely affected the insolubility of this material. Now, from the mode of its preparation, it is evident that a perfectly

* Composed of vaseline and beeswax.

† *Wied. Ann.*, xvii., p. 199.

‡ From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

neutral solution of citrate ammonia is practically unattainable, although the variations from neutrality must of necessity be of the minutest kind if proper care is used. These variations must either incline to alkalinity or acidity, but a little consideration would lead to the belief that, in almost every case (except where precautions are taken to insure the reverse) the inclination is to acidity.

I therefore prepared a solution of citrate of ammonia in the same manner as I conceived the majority of analysts, who did not know of the effect of this acidity, might prepare it. The directions in *Bulletin* No. 24, page 224, were followed with great care, and neutrality made by the addition of ammonia hydrate until the solution ceased to show acidity with blue litmus paper of great delicacy. Red litmus paper of great delicacy was also unaffected. I tried rosolic acid, but could do no no better. We will call the solution A. Another solution, B, was made by adding ammonia hydrate to a portion of A until it showed a very faint alkalinity with delicate red litmus paper. The quantity of ammonia hydrate necessary to do this was about 1 cubic centimetre of a solution of the strength of 22° Baumé, to 1 litre of the A solution. I also prepared, with a view of obtaining a comparison of the two methods, a solution, C, according to the directions of M. H. Joulie, making it, as directed, strongly alkaline.

Before trying these solutions on the aluminic phosphate, I was curious to see what differences in effect, if any, they would produce on calcium phosphate. One grm. of ground South Carolina rock containing 27 per cent P_2O_5 was taken in each experiment, and digested without attempting to remove the small quantity of water-soluble (if indeed any were present). The official method was carried out strictly as to time, temperature, &c., with regard to A and B; and Joulie's directions in everything except time, which was only one-half hour instead of one hour with regard to C, no heat being applied in this case, it being digested at the temperature of the laboratory. The following results were obtained in per cent of reverted P_2O_5—

	A.	B.	C.
	1·01	0·75	0·73
	0·90	0·73	0·74
	0·83	0·76	0·77
Mean ..	0·913	0·746	0·746

Three experiments were now made in every respect the same as above, except that all were digested one hour, the time specified in Joulie's method, and the following results in per cent of reverted P_2O_5 were obtained :—

	A.	B.	C.
	1·85	0·787	0·73
	1·83	0·74	0·78
	1·86	0·76	0·77
Mean ..	1·846	0·761	0·76

Five different portions of 1 grm. each were now digested in C for four hours, and I obtained the following percentages of reverted P_2O_5: 0·71, 0·78, 0·79, 0·70, 0·75. Mean of the five: 0·746, or the same as B and C gave when the substance was digested only half an hour.

There is great significance in the results thus obtained. The continuous dissolving action of the solution A is apparent, while both the B and C solutions cease to act as soon, apparently, as all the available P_2O_5 has been dissolved, which is within the first half hour; and an indefinite extension of the time of digesting, especially in the case of the C solution, seems to produce no further effect. Thus solutions B and C have been prepared, which, contrary to the generally accepted belief, will not go on continuously dissolving out P_2O_5 from calcium phosphate as long as any remains undissolved, provided enough time is allowed; and we have here (if, by further experiment, this is found by others to be true) a true measure of the availability of a phosphate, or at least a means of separating more sharply than we have hitherto been able to do soluble calcium phosphates from insoluble; and, with such a solution, which can be made by a very slight modification of the present official solution, the time element in the official method would cease to be an essential, as it is now, and would, in all probability, give much more accurate results, as well as conduce, more than anything else, to constancy and uniformity of results. From these experiments we perceive that a solution inclined to acidity, like solution A, tends, on calcium phosphate, to err on the side of too high a percentage of reverted phosphoric acid. The error is probably very small, but still that is the tendency. When, however, such a solution is used on aluminic phosphate, the reverse is the case to such an extent as to make the official method utterly worthless for the analysis of this material.

One grm. of the aluminic phosphate containing 47 per cent P_2O_5, with 34·74 per cent available P_2O_5, according to Stillwell and Gladding, was digested in each of the solutions A, B, and C, strictly following as to time, temperature, &c., the official method with A and B; and Joulie's method, except as to time, which was one-half hour, instead of one hour, with C. The water soluble, being insignificant in amount, was not removed before digesting. The following are the results obtained :—

	A.	B.	C.
	19·80	31·24	26·18
	19·90	33·44	27·63
	19·63	30·31	26·92
Mean ..	19·77	31·66	26·91

One grm. of the material was now treated in every respect the same as in the last experiments, except that the digestion was one hour instead of half an hour in all cases, and gave the following results, in per cent available P_2O_5 :—

	A.	B.	C.
	31·48	34·68	34·74
	32·11	34·79	34·72
	30·59	34·73	34·74
Mean ..	31·39	34·73	34·73

It seems incredible that two solutions differing so very slightly in composition as do the solutions A and B should give such widely divergent results, the difference between the mean of the three results obtained by solution A and the mean of the three obtained by solution B by digesting half an hour, being no less than 11·89 per cent available P_2O_5. The lack of concord in the results obtained by each solution separately, together with the wide differences in the means of the results obtained from the three solutions, suggest the conclusion, however, that in the case of each solution, the official time (half an hour) was insufficient to dissolve the material.

By digesting one hour, concordant and uniform results are obtained by solutions B and C. The results from A are still very much lower than B, although the difference is not so great as it was in the previous experiments. I found that the material was capable of being almost completely dissolved in all three solutions, if sufficient time was given.

(To be continued.)

On Metaphenyltoluene.—G. Perrier.—Of the three phenyltoluenes theoretically possible, the ortho-compound has been studied by Barbier and the para-compound by Carnelley and Thomson. To obtain the meta-compound the author causes metabromotoluene to act upon phenylbromide in presence of an excess of sodium.—*Bull. Soc. Chim. de Paris*, No. 6, 1892.

ON THE

APPLICATION OF THE SAFETY LAMP TO THE DETECTION OF BENZOLINE VAPOUR AND OTHER INFLAMMABLE VAPOURS IN THE AIR.*

By FRANK CLOWES, D.Sc. (London),
Professor of Chemistry, University College, Nottingham.

Since the vapour of benzoline and of petroleum spirit, when mixed with air, may become dangerously explosive and inflammable, it is found necessary to employ safety-lamps instead of naked lights to illuminate spaces which may contain such a mixture. The safety-lamp should accordingly be used in the neighbourhood of the oil tanks in petroleum-carrying steamers, in petroleum stores, and in chambers in which processes are carried on which involve the use of light petroleum oil.

The suggestion naturally occurs that the safety-lamp used in these places should be applied to ascertain whether the amount of inflammable vapour present in the air is sufficient to give rise to danger if it should come into contact with the naked flame; in other words, to ascertain if the space is sufficiently ventilated. Experiments were accordingiy undertaken to discover whether benzoline vapour would give rise to a "cap" over the flame of the safety lamp, and if a "cap" appeared, to discover how small a proportion of the vapour could be detected in air by this flame-cap test. Since the hydrogen flame in the safety-lamp, and the benzoline flame in Ashworth's modified lamp, had been found to be most convenient for the formation of visible "caps," these lamps were employed in the experiments; and the test chamber previously described was employed for exposing the lamps to mixtures in varying proportions of benzoline vapour with air.

Since benzoline is a mixture of liquids, and is therefore not of invariable chemical composition, no attempt was made to ascertain the actual percentage of the vapour present in the air. The percentages of vapour, even if known and identical in amount, would probably have different effects when derived from different samples of benzoline, or even when derived from the same samples under different conditions. Accordingly an approximate determination only was made of the amount of further dilution with air which an explosive or inflammable mixture might undergo before the "cap" it produced over the safety-lamp flame ceased to be easily visible.

A large gas-holder was filled with air which had bubbled through benzoline, and was thus charged with the vapour at the ordinary temperature, in the same way as air would be charged with the vapour from the evaporation of stored benzoline. This mixture was inflammable when kindled in the open air. Varying proportions of this mixture with additional air were then prepared, and the effect was ascertained of introducing a flame into them. It was found that a mixture of 1 volume of benzolised air with 4 volumes of air was violently explosive. When the proportion of air was increased from 4 to 7 volumes the mixture was still inflammable, and when the air was increased to 9 volumes the mixture ceased to be inflammable. Mixtures of the same benzolised air were then made in the test chamber with still larger proportions of air, and the appearance of the safety-lamp flames was examined in these mixtures, with the results shown in table.

The results of these experiments showed that the 10 m.m. hydrogen flame in the Ashworth safety-lamp will detect a quantity of benzoline vapour in air which is only $\frac{1}{15}$th that of the explosive proportion, and $\frac{1}{30}$th of that which is inflammable when mixed with air. The benzoline flame shows a very small but distinct "cap" when the amount of benzoline vapour is $\frac{1}{4}$th that requisite for production of an explosive mixture, and $\frac{1}{8}$th that will yield an inflammable mixture.

* A Paper read before the Royal Society.

Proportion of benzolised air to air in mixture.	Behaviour of the mixture with a naked flame.	Appearance of the hydrogen "cap" over safety-lamp flame in the mixture.
1 : 4	Violently explosive.	
1 : 5	Burns rapidly, and would probably be explosive if fired in large quantity.	
1 : 6		
1 : 7		
1 : 8	Burns around a flame only.	
1 : 9	Non-inflammable.	
1 : 23	,,	52 m.m. "cap."
1 : 36	,,	43 ,, ,, / 4 ,, ,, with benzoline flame.
1 : 72	,,	31 m.m. "cap."
1 : 144	,,	22 ,, ,,

Further experiments of a similar kind are being made with the vapour of alcohol and of ether.

I have to acknowledge with pleasure the valuable manipulative skill and fertility of resource of W. T. Rigby, who has assisted me in carrying out the experiments with the test chamber.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 30th, 1892.

Prof. A. Crum Brown, F.R.S., President, in the Chair.

The President delivered an Address, of which the following is an abstract:—

The number of Fellows of the Society is 1855, including 30 foreign members, 120 Fellows having been admitted during the year.

The Society has to deplore the loss of two veteran foreign members, Hermann Kopp and Jean Servais Stas. The Treasurer has undertaken to give an account of the work of the former, and to sketch the modern development of his ideas in a lecture to be delivered during the coming session. It is hoped that in like manner justice may be done to the work of Stas by one of the Fellows specially qualified to deal with such a subject.

The following tabular statement gives the numerical position of the Society:—

Number of Fellows (Anniversary, March, 1891) ..			1754
Since elected and paid admission fees			120
			1874
Removed on account of arrears	18		
Withdrawn	18		
Deceased	13		
			49
Present Number of Fellows			1825
Number of Foreign Members (1891) . ..	32		
Deceased	2		
Present number of Foreign Members			30

13 Fellows have died within the year:—Dr. J. H. Abrahall, Dr. A. J. Bernays, Chas. Heisch, H. J. Hardy, T. H. Hills, J. S. Jackson, J. B. Mackintosh, C. McNally, J. W. Pratt, Dr. Redwood, A. J. Shilton, Dr. Tidy and P. H. Wright.

18 Fellows have withdrawn:—H. H. Bunting, W. L. Clarke, W. Y. Dent, Rev. G. R. Faulkner, Robt. Ferguson, Thos. Hilditch, Rev. T. Lindsay, Wm. Robinson, J. B. Readman, W. H. Reid, Chas. T. Sprague, George

Sutcliffe, C. H. Sieber, Samuel D. Wills, J. C. Watson, W. C. Wise, Prof. E. Marks, and D. T. C. Charles.

18 Fellows have been removed on account of arrears: T. S. Conisbee, W. Crossley, Albert Cobb, Ed. Dawson, Chas. Hulke, Wm. Houlding, H. E. J. Irons, A. J. G. Lowe, Rev. S. Langdon, Eberhard Luttgen, Jas. Mayne, E. W. Parnell, Wm. Rupp, S. A. P. Szczepanowski, Edward de Souza, Arthur Stanley, W. B. Turner, and T. E. Towerson.

No fewer than 128 papers have been read, the largest number on record. The 1891 volume of the *Chem. Soc. Trans.* contains 95 original papers, occupying 1100 pages, while the Abstracts occupy 1564 pages.

At the commencement of the winter session Professor Attfield brought under the notice of the Council his proposal for establishing a Chemists' Benevolent Fund, A Committee was appointed to consider this proposal, and eventually they presented their Report (see p. 157), stating that it represented their unanimous opinion.

This Report was considered and adopted by the Council, and by their unanimous vote it was resolved:—

"That the Report of the Committee on the proposed institution by the Chemical Society of a 'Chemists' Benevolent Fund' be received and entered upon the Minutes.

"That in view (*a*) of the claims of scientific chemists on the Relief Fund of the Royal Society; (*b*) of the difficulties that would attend the establishment and satisfactory administration of a separate Fund by the Chemical Society; and (*c*) of the conditions affecting the particular scheme, Prof. Attfield's proposal for the establishment of a 'Chemists' Benevolent Fund,' in connection with the Chemical Society, be not entertained.

"That a copy of this Resolution be forwarded to Prof. Attfield, with an expression of thanks to him personally for the unsparing efforts he has made in the matter, and to the promised contributors to the suggested Fund for their generously proffered support thereto."

A Committee of the Council have had under consideration the question of the entire rearrangement, ventilation, and lighting of the meeting room, and with the co-operation of Professor Ayrton and Mr. Martin L. Saunders (architect) have prepared a scheme which is now under the consideration of Her Majesty's Office of Works; if approved, this will be carried into effect during the long vacation.

In the remainder of his Address, the President dwelt chiefly on the work which is being done on the border lines of chemistry proper—referring both to that by which an approach is gradually being made towards understanding the chemistry of Nature's organic laboratory; and to the application of mathematical and physical methods of inquiry to the solution of chemical problems.

Sir Henry Roscoe proposed a vote of thanks to the President, coupled with the request that he allow his Address to be printed. Dr. Gladstone seconded the motion, which was carried by acclamation. The President having thanked the meeting,

Prof. Thorpe, the Treasurer, gave an account of the balance sheet, which he laid before the Society duly audited. The receipts had been:—By admission fees and subscriptions, £3545; by sale of Journal, £408 7s. 4d.; and by dividends on invested capital, £367 12s. 10d. The expenses had been:—On account of the Journal, £2798 15s. 10d.; on account of the *Proceedings*, £159 14s. 5d.; on account of the Library, £277 6s. 2d.; the total expenditure being £3989 1s. 6d. Grants amounting to £406 5s. 4d. had been made to Fellows from the Research Fund during the year. As illustrating the growth of the Society's work, the Treasurer mentioned that whereas the expenditure on the Journal had been only £1733 11s. 10d. in 1882, in 1887 it had risen to £2026 16s. 9d., and this year amounted to £2798 15s. 10d. He anticipated that the proposed alterations and re-decorations of the Society's rooms during the coming long vacation would absorb nearly £1000 of the balance now at the bank.

Mr. David Howard proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Prof. E. Frankland.

Sir Henry Roscoe having asked for information with reference to the Report of the Jubilee Meeting, and with regard to the Learned Societies' Registration Bill, both items of charge in the balance sheet, Dr. Armstrong said that the former was in hand, and would ere long be ready for issue; unfortunately they had been unable to induce any Government Department to take charge of the Registration Bill, and he feared that there was but little chance of getting it brought forward unless promoted as a private measure.

Mr. Cassall, after a reference to the cost of printing the suggested alterations in the bye-laws, which he supposed was included in the cost of printing the *Proceedings*, asked the President whether he had received a letter, and was prepared to consider the request therein made that he would inspect the documents in which a number of Fellows of the Society had expressed their wishes with reference to the suggested alterations in the bye-laws.

The President replied that he had received a letter signed by Dr. Teed and Mr. Cassall, and that he could only say that a letter from even one Fellow of the Society would meet with every consideration from him.

The vote of thanks to the Treasurer having been passed, the Treasurer proposed a vote of thanks to the Auditors, mentioning that he was much indebted to Mr. Tutton for his assistance in connection with the accounts. Prof. Ramsay seconded the motion, which was unanimously adopted, and acknowledged by Mr. Dyer.

Prof. Odling then a proposed a vote of thanks to the Council and Officers, including the Editors, Abstractors, and Librarian. Mr. Carteighe supported the motion, which was adopted. Dr. Armstrong and Mr. Groves having replied,

Scrutators were appointed, and a ballot was then taken for the election of Officers and Council for the ensuing year; the following were subsequently declared elected.

President—Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—A. Vernon Harcourt, F.R.S.; W. N. Hartley, F.R.S.; John Pattinson; William Ramsay, F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries—H. E. Armstrong, Ph.D., F.R.S.; J. Millar. Thomson, F.R.S.E.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council—Henry Bassett; Norman Collie, Ph.D.; Harold Dixon, F.R.S.; John Ferguson, M.A.; R. J. Friswell; John Heron; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; John A. Voelcker, Ph.D.; W. P. Wynne, B.Sc.

Correction of a "Note on a New Acid from Camphoric Acid." By W. H. Perkin, jun., F.R.S. (*ante*, p. 165).

The author desires to express regret that he had overlooked a previous paper by Damsky (*Ber.*, 1887, 2964), in which an account is already given of the acid recently described by him as new.

April 7th, 1892.

Dr. W. H. PERKIN, F R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. Frederick William George Blyth, Clifton Wood, Clifton, Bristol; George Fitz-Brown, Ditton, Widnes; Walter William Duffield, 24, Ursula Street, Battersea, S.W.; Walter N. Edwards, 4, Herne Hill Road, Camberwell, S.E.; Harold F. Hills, 149, Bow Road, London, E.; John H. B. Jenkins, 23, Harding Street, New Swindon; Albert Morris, 115, Hope Street, Dukinfield; Joseph Chas. Mulrenan, 45, Manor Road, Stoke Newington, N.; Wm. Herbert Stables, B.A., Glebe House, Kirkstall, Leeds; Laurence John de Whalley, B.Sc., 26, Park Place, Greenwich.

Of the following papers, those marked * were read:—

*1. "*The Separation of Arsenic, Antimony, and Tin.*" By JOHN CLARK, Ph.D.

The mixed sulphides of arsenic, antimony, and tin, obtained in the ordinary course of analysis are dissolved in a strong solution of ferric chloride in chlorhydric acid, and the arsenic is distilled off and weighed as trisulphide. The residual liquid contains the antimony as trichloride, and the tin as stannic chloride, also ferrous and ferric chlorides. The author corroborates Loveton's statement that antimony and tin can be separated by taking advantage of the difference in solubility of their sulphides in solutions of hydrogen chloride of certain strengths, but thinks the proportion of acid should be reduced from a half to a third, to ensure the complete precipitation of the antimony, and to avoid the necessity of filtering through cotton-wool. He recommends a combination of Loveton's and F. W. Clarke's processes, and without removing the iron salts he precipitates the antimony with hydrogen sulphide in a tepid solution containing from $\frac{1}{3}$ to $\frac{1}{2}$ of its volume of chlorhydric acid and a considerable quantity of oxalic acid. The precipitate, which is free from tin, is washed first with water, then with alcohol, and finally with carbon bisulphide, and weighed as Sb_2S_3 after being heated at a temperature of about 130° to ensure the complete expulsion of water. He considers this temperature sufficiently high to dry the Sb_2S_3. He points out that when Sb_2S_3 is dried at 130° it suffers little or no further loss in weight till it is raised to the temperature at which it is converted into the black sulphide, and his experiments indicate that the loss in weight observed at this stage is not due to water but to oxidation, as after heating between 200° and 230° for several days there was a continuous loss, the black sulphide becoming brown, and it was found by analysis to consist chiefly of oxide of antimony.

When the Sb_2S_3 precipitate is large it is necessary, after drying, to digest it in carbon bisulphide to extract the whole of the sulphur. To obviate this objection the author reduces the excess of ferric chloride with thin sheet-iron, and as soon as the yellow colour has disappeared the undissolved iron is removed, and the antimony which has come down is re-dissolved with the aid of a little ferric chloride, which is added drop by drop till the solution is distinctly yellow to ensure that all the tin is in the stannic state; a warm solution of oxalic acid containing about one third of its volume of chlorhydric acid is then added, and the antimony is precipitated as Sb_2S_3, together with traces of sulphur, and washed with water, alcohol, and carbon bisulphide.

After the removal of the antimony the hydrogen sulphide is expelled by boiling, the oxalic acid decomposed with potassium permanganate, and the tin precipitated in a hot solution with hydrogen sulphide, and allowed to stand till cold. The SnS_2 obtained in this way can be filtered off and washed with water without passing through the filter. It is then converted, by ignition, into SnO_2, in which form the tin is weighed. The test analyses are very satisfactory.

For qualitative purposes, in distilling off the arsenic, a condenser is not necessary, a bent tube dipping into water being sufficient. It is advisable, however, to use a safety-tube to prevent the distillate coming back.

In the case of alloys the metal is dissolved in strong chlorhydric acid with the aid of ferric chloride, and the arsenic distilled off at once. The antimony and tin, after being separated from the other metals of the group, are then estimated in the manner described above.

*2. "*Platinous Chloride and its Use as a Source of Chlorine.*" By W. A. SHENSTONE and C. R. BECK.

The authors have examined chlorine from six specimens of platinous chloride of independent origin, and have found oxygen and hydrogen chloride to be present in them all. From these results they conclude that platinous chloride made by any of the processes hitherto recommended, including that lately suggested by L. Pigeon, contains a very perceptible quantity of some basic compound, which gives off water together with the gases previously mentioned.

They have noticed that after mercury has been exposed to the action of chlorine in the presence of a trace of water, it becomes capable of absorbing hydrogen chloride; it is not yet certain whether this action depends on the presence of oxygen or not.

*3. "*Note on the Adhesion of Mercury to Glass in the Presence of Halogens.*" By W. A. SHENSTONE.

The author finds that carefully purified chlorine, bromine, and iodine affect mercury like ozone, causing it to adhere to glass in a remarkably perfect manner.

*4. "*The Decomposition of Mannitol and Dextrose by the Bacillus Ethaceticus.*" By PERCY F. FRANKLAND, F.R S., and JOHN S. LUMSDEN.

The products of the fermentation of both these compounds consist of ethyl alcohol, acetic acid, carbonic anhydride, hydrogen, and traces of succinic acid. When the fermentations are conducted in a closed space there is invariably also a considerable quantity of formic acid produced, whilst in fermentations in an open space (flasks plugged with cotton-wool) formic acid, except in traces, is a most exceptional product. The same phenomenon has been already pointed out by one of the authors in the case of a fermentation with another organism (*B. ethacetosuccinicus*), and it is, doubtless, due to formic acid being one of the primary products of the fermentation, and then breaking up, more or less completely, into equal volumes of carbonic anhydride and hydrogen. This decomposition is, however, retarded when the products —carbonic anhydride and hydrogen—are prevented from escaping, as is the case in fermentations conducted in a closed space. Indeed, the proportion in which the carbonic anhydride and hydrogen were found coincides almost exactly with that in which they are present in formic acid. The proportions in which the several products are obtained from mannitol is approximately represented by the equation:—

$$3C_6H_{14}O_6 + H_2O = C_2H_4O_2 + 5C_2H_6O + 5CH_2O_2 + CO_2,$$

whilst in the case of the dextrose the products occur in the proportions:—

$$2{\cdot}5C_2H_6O : 1{\cdot}5C_2H_4O_2 : 3CH_2O_2 : CO_2.$$

Thus, there is more acetic acid in proportion to alcohol and formic acid produced in the case of dextrose than in that of mannitol. The carbon dioxide given among the products really represents that liberated from the calcium carbonate present in excess by a fixed acid insoluble in ether, the nature of which could not be determined.

The fermentations conducted in a closed space are always found to be markedly less complete than those which take place in an open one.

There is a close qualitative and quantitative resemblance between these fermentations by the *B. ethaceticus* and those previously described by one of the authors as taking place through the agency of the *Pneumococcus* (Friedländer), which renders it probable that this ethacetic

decomposition is a very general and typical form of fermentative change.

DISCUSSION.

Dr. ARMSTRONG, after remarking on the interest attaching to the discovery of formic acid, in considerable quantity, among products of fermentation, said that he could not think the explanation satisfactory which the authors had advanced of the non-production of this acid when closed flasks were used, viz., that the breaking up of the acid into hydrogen and carbon dioxide, which took place when fermentation was conducted in open vessels, was retarded by their presence when the products were prevented from escaping: that such an influence could be exerted on a fermentation from without was scarcely probable, according to present knowledge. It was more likely that there were distinct initial differences between fermentations carried on under the two sets of conditions.

Professor FRANKLAND, in reply, said that he thought the difference might be attributable to a difference in pressure involved in collecting the gases, in the one case, over mercury, rather than to absence of air, and he was, therefore, at present studying the influence of pressure.

In reply to a question by Dr. Kipping, he added that it was very remarkable that, notwithstanding both alcohol and acetic acid were formed, no trace of ethylic acetate could be detected among the products.

*5. "*The Preparation of Glycollic Acid.*" By H. G. COLMAN.

Glycollic acid may be readily prepared by boiling a concentrated solution of potassium chloracetate for 24—30 hours in a flask connected with a reflux apparatus. The product, which consists of a solution of glycollic acid and potassium chloride, is distilled under reduced pressure, the temperature in the distilling flask not being allowed to rise above 70°, and the residue is mixed with a large quantity of acetone, filtered from the separated potassium chloride, and the acetone solution concentrated. Glycollic acid soon separates out in colourless crystals, which only contain 0·5 per cent of ash, and are sufficiently pure for most purposes. The yield is about 85 per cent of the theoretical.

Glycollic anilide, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_2OH$, may be prepared by heating glycollic acid for some time at 240°, boiling the residue with aniline, and re-crystallising the product from water. It has the properties assigned to it by Norton and Tscherniak (*Bull. Soc. Chim.*, xxx., 104). Attempts were made to convert this compound into oxindole—

$$C_6H_4\!<\!\begin{matrix}CH_2\\NH\end{matrix}\!>\!CO,$$

by eliminating the elements of water, but without success. Phosphorus pentoxide acts on the anilide, but the crystalline product consists simply of the phosphate $PO(O{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}Ph)_3$.

According to measurements made by Mr. W. J. Pope the crystals of glycollic acid obtained from an acetone solution belong to the orthorhombic system, $a:b:c$ = 0·774 : 1 : 0·368, and exhibit the macropinacoid (100), the brachypinacoid (010), the macrodome (101), and the prism (110). Glycollic acid would seem to be dimorphous, as Groth has described (*Krys. Zeit.*, v., 309), crystals of the acid obtained from aqueous solution, which belongs to the monosymmetric system. Glycollic anilide crystallises in the monosymmetric system, $a:b:c$ = 0·9322 : 1 : ?; β = 64° 55′, and show the orthopinacoid (100), the basal pinacoid (001), and the prism (110).

6. "*Researches on Silicon Compounds and their Derivatives.* Part VI. *The Action of Silicon Tetrachloride on Substituted Phenylamines.*" By J. EMERSON REYNOLDS, D.Sc., F.R.S.

In Part V. of this investigation the author described some members of a class of silicon compounds of the type $Si(RNH)_4$, obtained by the interaction of silicon tetrabromide and tetrachloride and aniline, ortho- and para-toluidine and α- and β-naphthylamine; the action of a silicon haloid on the secondary and tertiary alkaloids diphenylamine, ethylaniline, and diethylaniline is now described.

Diphenylamine, when free from extraneous matter capable of decomposing silicon chloride, combines with the latter to form an unstable addition compound, which is decomposed below the boiling-point of benzene. No interaction with the silicon haloid was obtained analogous to that which readily occurs with phenylamine.

Ethylaniline, on the contrary, is easily acted on by silicon chloride, ethylaniline chlorhydride separating, a liquid product being obtained containing the new compound $Si(PhNEt)_4$.

Diethylaniline, when pure, is but feebly acted on by silicon tetrachloride even when heated with it at 190° under pressure; no ethyl chloride separates, but the compound $PhNEt_2HCl$ is formed together with a liquid which probably contains the compound $Si(C_6H_5NEt_2)_4$.

It appears, therefore, that the substitution of phenyl for but one atom of hydrogen in aniline confers on the resulting alkaloid greater immunity from attack by silicon tetrachloride than displacement by ethyl of part or all the amidic hydrogen of aniline.

7. "*Chemistry of the Compounds of Thiourea and Thiocarbimides with Aldehyd-Ammonia.*" By AUGUSTUS E. DIXON, M.D.

In a previous paper (*Chem. Soc. Trans.*, 1888, 411) the author showed that the alkyl and allied thiocarbimides and aldehyd-ammonias interact in accordance with the equation:—

$$R{\cdot}NCS+2R'CH(OH)NH_2=CSN_2H_2R(CHR')_2+2H_2O,$$

and the possibility was suggested of a connection between the class of substances so formed and a compound obtained by Nencki (*Ber.*, vii., 162) by the action of thiourea on aldehyd-ammonia.

The principal general results established by a continuation of this investigation are that Nencki's compound, a homologue of the latter (obtained from thiourea and valeraldehyd-ammonia), and the thiocarbimide derivatives formed in accordance with the equation above given, agree in properties in the following respects:—

(1) They combine with picric acid in equimolecular proportions.

(2) They are decomposed by hot acetic anhydride, with separation of both aldehyd groups, together with one of the three nitrogen atoms, the corresponding acetylated thiourea being formed; while (3) boiling with water effects an analogous decomposition, save that the resultant thiourea is non-acetylated.

(4) They combine with silver nitrate, forming sparingly soluble addition products, which are more or less unstable in presence of water.

From this similarity in behaviour the inference is drawn that they are members of the same class.

Though thiourea and aldehyd-ammonia readily interact this was not found to be the case when substituted thioureas were employed; under no circumstances (and the experiments were conducted under a great variety of conditions), was any sign of combination observed. This inertness is difficult of explanation if the monosubstituted thioureas possess the structure—

$$CS\!<\!\begin{matrix}NHR\\NH_2\end{matrix},$$

but is intelligible on the supposition that they are of the form—

$$HN{:}C\!<\!\begin{matrix}NH_2\\SH\end{matrix}.$$

Evidence in favour of the latter formula has already been adduced from a slightly different point of view by Prof. Emerson Reynolds (*Chem. Soc. Trans.*, 1891, 394), who, further, considers it probable that the substituting radicle displaces hydrogen in the imidic group.

The following compounds, amongst others, are described:—

Thiourea and valeraldehyd-ammonia, $CSN_3H_3(C_5H_{10})_2$ —flattened, rhombic crystals, insoluble in water, and melting between 120° and 121° (uncorr.).

Methylthiocarbimide and acetaldehyd ammonia, $CSN_3H_2Me(CHCH_3)_2$—white needles, soluble in water and alcohol; melting-point 142° to 143° (uncorr.).

Acetylthiocarbimide and aldehyd-ammonia, $CSN_3H_2Ac(CHCH_3)_2H_2O$ —slender needles, soluble in water and alcohol; melting-point 187° (uncorr.).

Phenylcarbimide and aldehyd-ammonia, $CON_3H_2Ph(CHCH_3)_2$ —satiny needles, insoluble in water, sparingly soluble in alcohol; melting-point 199° to 200° (uncorr.).

8. "*The Atomic Weight of Boron.*" By J. L. HOSKYNS-ABRAHALL, B.A., Ph.D., late Bishop Berkeley Fellow of the Owens College. (Edited by T. Ewan and P. J. Hartog, of the Owens College.)

The deceased author determined the atomic weight of boron by estimating the amount of silver necessary to precipitate the bromine of a known weight of boron bromide. The editors have drawn up from the notes of the almost completed research a memoir which will shortly be submitted for publication. The results of the final series of determinations are as follows:

Number of bulb.	Weight of BBr_3.	Weight of Ag.	Ratio of BBr_3 to Ag.	Atomic weight of boron (O=16).
19.	1·65511	2·13759	0·774288	10·838
23.	4·46783	5·77127	0·774153	10·794
25.	8·42315	10·88065	0·774146	10·792
11.	7·72194	9·97405	0·774203	10·811
32.	4·09274	5·28595	0·774268	10·831
10.	8·03235	10·37420	0·774262	10·829
			Mean error =	0·017.

The mean atomic weight is 10·816; the probable error being 0·0055.

The atomic weight obtained by taking the total of the mean weights of boron bromide and of silver used in the series of determinations is 10·811.

The atomic weights used in the calculation are Ag=107·923, Br=79·951. (Clarke, "Constants of Nature.")

It is to be noticed that an experimental error of 1 part in 1000 in the determination of the ratio of boron bromide to silver will produce an error of 23 parts in 1000 in the atomic weight, owing to the small percentage of boron present in boron bromide.

NOTICES OF BOOKS.

Laboratory Practice: A Series of Experiments on the Fundamental Principles of Chemistry. A Companion Volume to "The New Chemistry." By JOSIAH PARSONS COOKE, LL.D., Erving Professor and Director of the Chemical Laboratory, Harvard University. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1892. Small 8vo., pp. 192.

THE first point which here strikes us is that this book, though printed and published in England and intended for English students—or, at least, likely to fall into their hands—contains matter intelligible only to readers conversant with American conditions. We are told that a "farina kettle" is a good steam bath, and that the "quick-sealing fruit or milk jars" are good gas-holders. But farina kettles and quick-sealing fruit-jars are not commonly to be met with on this side the Atlantic. Nor with us are balances and thermometers necessarily imported from Germany. Elsewhere we are told to "use a half-pint *tincture* (?) of thin glass."

We find a plate representing a kerosene stove and tube furnace, the former curiously labelled "Chemical American." Such plates are merely waste paper in a country where gas is available in every laboratory. The teachings of the book are judicious, and it might be undoubtedly recommended if it had only been remodelled in accordance with English conditions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 14, April 4, 1892.

Native Iron of the Canon Diablo.—M. Mallard.—Fragments of native iron had been discovered in March, 1891, near the Canon Diablo, in Arizona. One of these specimens was submitted to the examination of Prof. Kœnig and was found extremely hard. A freshly cut surface was found interspersed with small cavities, filled with black matter and containing diamonds, one of which had a diameter of 0·5 millimetre and scratched corundum with extreme ease. The iron contained only 3 per cent of nickel; the black matter seemed to be iron carbide. In two of the cavities there were blackish grains which even scratched the cleavages of white diamond. They were probably "carbonado,"—a black diamond.

Electric Spectra of Gallium.—Lecoq de Boisbaudran.—The substance of this memoir consists of tabular views of the rays obtained. The author remarks, in conclusion: "We see what curious changes the spectrum of gallium undergoes if the nature of the spark is caused to vary. As analogous changes are produced in a more or less remarkable manner with almost all substances it is very necessary to define the conditions under which electric spectra have been obtained."

The Production in the Dry Way of Some Anhydrous Crystalline Sulphates.—P. Klobb.—The substances thus obtained are zinc sulphate, anhydrous copper, cobalt and nickel sulphates.

Nitroketone derived from the Camphosulphophenols.—J. Cazeneuve.—The two isomers, amethylcamphophenolsulphone and amethylcamphophenolsulphonic acid, undergo a remarkable transformation. The sulphur connected to the nucleus resists concentrated hydrochloric acid and boiling potassa-lye, but in contact with nitric acid it is set free in the state of sulphuric acid whilst the group NO_2 is substituted. The mol. also loses 2H in the state of water.

On the Composition of Pinnaglobine.—a Novel Globuline.—Dr. A. B. Griffiths.—Already inserted.

Journal fur Praktische Chemie.
Vol. xliv., Nos. 21 and 22.

Researches from the Laboratory of A. Weddige.—These comprise a very extensive memoir on the action of sulphonic acid chlorides upon orthoamidabenzamide by Ernst Franke.

Researches from the Laboratory of the University of Freiberg.—Here are included a paper by Ad. Claus and Howitz on the action of bromine upon para- and oxyquinoline; a memoir by C. Willgerodt and E. G. Mühe on picrylic, orthoparadinitrophenylic, and nitroazo- or nitronitrosoazometachlorphenylhydrazine and their derivatives, including a tabular view of the formulæ, colours, forms, melting-points, decomposition points, and

solubilities in water, alcohol, glacial acetic acid, benzene, ether, and chloroform, of 26 compounds, and a paper on paranthracen by Karl Elbs, in which the author states that derivatives of paranthracen have not yet been obtained by means of any reagent.

On a Method for Determining the Constitution of Saturated and Non-Saturated Haloid Derivatives and Hydrocarbons.—Mejer Wildermann.—This paper does not admit of useful abridgment.

Action of Oxidising Agents upon Aliphatic Thioureas.—D. S. Hector.—In two earlier papers the author has published in the *Berichte* (xxii., p. 1176, and xxiii., p. 357) his researches on the behaviour of the aromatic substituted thioureas with oxidising agents, especially with a three per cent solution of hydrogen peroxide. He now extends these investigations to certain thioureas of the aliphatic series, and to allylic-methylic and to simple thiourea. The reaction which occurs on the oxidation of the aromatic thioureas with hydrogen peroxide in an acid solution takes place also when aliphatic thioureas are treated with the same oxidising under the same conditions, but it is completed only to the extent of one half.

On Two New Selenious Salts.—R. Schneider.—The salts are the potassium seleno-stannate and the corresponding sodium salt.

An Explanation.—Ad. Claus.—The author declines to continue the controversy with Herr Michael as devoid of interest.

Bulletin de la Société Chimique de Paris.
Parts vii. and viii., No. 5, March 5, 1892.

Determination of the Congelation-Point of very Dilute Aqueous Solutions. Application to Cane-Sugar.—F. M. Raoult.—The author has determined the lowering the freezing-points of solutions of cane-sugar, taking in preference the most highly diluted.

Separation and the Determination of Lead, Silver, and Zinc, in Ores composed of Galena and Blende.—Emile Aubin.—Already noticed.

Action of Propyl Iodide upon Pure Trimethylamine in Aqueous Solution, and in Equimolecular Proportions in the Cold. Trimethylpropylammonium Iodide.—H. and A. Malbot.—This process is much more rapid than that of isoamyl iodide, and especially than that of isobutyl iodide. In 18 hours the ether has almost completely disappeared.

Action of Isopropyl Iodides upon Pure Trimethylamine in Aqueous Solution, and in Equimolecular Proportion in the Cold and at 100°. Trimethylisopropylammonium Iodide.—H. and A. Malbot.—The action of heat does not interfere with the normal reaction, as it occurs in the cold. In each case the result is the entire conversion of the isopropyl iodide and of the trimethylamine into trimethylisopropylammonium.

Action of Allyl Iodide upon Pure Trimethylamine in Aqueous Solution and in Equimolecular Proportion. Trimethylallylammonium Iodide.—H. and A. Malbot.—If trimethylamine is allowed to fall drop by drop into allyl iodide it occasions slight explosions, as does bromine.

The Rotatory Power in Silks of Different Origins.—Leo Vignon.—The author has already shown that silks if examined in certain solvents exert a considerable rotatory power upon polarised light. He applies the differences to a determination of different kinds of silk.

Revue Universelle des Mines et de la Metallurgie.
Vol. xvii., No. 2.

This issue does not contain any chemical matter.

MEETINGS FOR THE WEEK.

MONDAY, May 2nd.—Medical, 8.30. (Annual Oration).
—— Society of Chemical Industry, 8. "The Distillation of Wood," by Prof. W. Ramsay, F.R.S., and J. C. Chorley. "Notes on the Composition of some Indian Gums of Known Origin," by Dr. S. Rideal.
— Royal Institution, 5. (Annual Meeting).
—— Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Theories," by Percy F. Frankland, F.R.S. (Cantor Lectures).
TUESDAY, 3rd.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Sculpturing of Britain—its Later Stages," by Prof. T. G. Bonney, D.Sc., F.R.S.
—— Pathological, 8.30.
WEDNESDAY, 4th.—Society of Arts, 8. "The Bradford Corporation Electricity Supply," by W. H. Preece, F.R.S.
THURSDAY, 5th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Chemistry of Gases," by Prof Dewar, F.R.S.
—— Chemical, 8. Ballot for the Election of Fellows.
FRIDAY, 6th.—Royal Institution, 9. "The Sensitiveness of the Eye to Light and Colour," by Capt. Abney, F.R.S.
—— Geologists' Association, 8.
—— Quekett Club, 8.
SATURDAY, 7th.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

ERRATA.—P. 203, foot of col. 2, the formula for pinnaglobine should read $C_{736}H_{964}N_{188}MnS_4O_{210}$, and *for* "$NO_3$" *read* "NO."

NEW PUBLICATIONS.

THE TANNINS; a Monograph on the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents, with an Index to the Literature of the subject. By HENRY TRIMBLE, Ph.M. Vol. I., crown 8vo., cloth. 10s. 6d.

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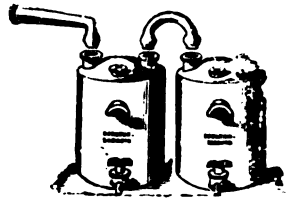

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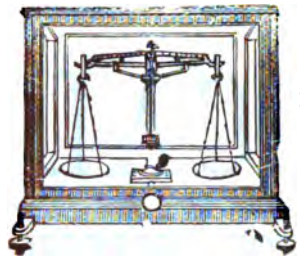

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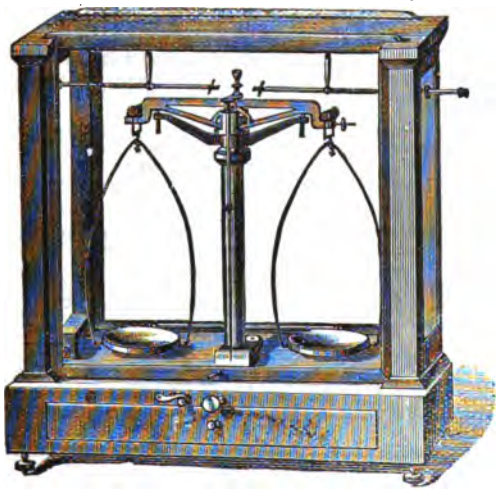

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THE CHEMICAL NEWS.

Vol. LXV., No. 1693.

PRELIMINARY NOTE ON THE YELLOW CRUSTS OF THE *FUMAROLE* IN THE CRATER OF VESUVIUS, AND THE NEW METAL VESBIUM.

By DR. T. L. PHIPSON,

Graduate of the Faculties of Science and Medicine of the University of Brussels, Fellow of the Chemical Societies of London, Paris, Antwerp, &c.

Formerly I discovered notable quantities of selenium in the arseniferous sulphur of Puzzuoli, near Naples (1862). I have lately examined the lava and yellow crusts of the *fumarole* from the crater of Vesuvius (specimens taken in 1879), and have found, besides the substances usually met with in volcanic products, considerable quantities of *fluorine*, which appears to have escaped the notice of Sylvestri, and minute quantities of *molybdenum*, which has perhaps given rise to the belief that a new metal, vesbium, exists in the yellow and green crusts of some ancient lava of Vesuvius, as described by the veteran observer A. Scacchi.

I have also found notable quantities of fluorine in the black lava (with white grains of leucite) of 1864; and it will probably be found that *fluoride of silicium* escapes with the dense white steam which issues from these apertures.

Since my distinguished friend, the late Prof. Nicklès, of the Faculty of Science of Nancy, showed that concentrated sulphuric acid, heated with rocks supposed to contain fluorine, would attack and corrode plates of glass when no fluorine was present, and that to make use of this familiar test it is absolutely necessary to use plates of polished quartz, and, moreover, since fluorine will escape in these circumstances from siliceous minerals in the form of fluoride of silicium which does *not immediately* attack either glass or quartz, I have had to find some method which would give accurate results and avoid the use of quartz plates, which are expensive. I have got over the difficulty thus:—To a few grms. of the pulverised rock in a very small glass beaker concentrated sulphuric acid is added, and the beaker covered with a clean glass plate. Another beaker exactly similar containing the same quantity of sulphuric acid, but no rock, and covered with a similar glass plate, is placed alongside as a *witness*, and the two are left thus at the ordinary temperature of the laboratory for the space of three days. At the end of that time the glass plate over the fluoriferous rock will be found corroded, whilst the other remains quite bright. This interval is necessary when fluo-silicic gas is chiefly evolved; with minerals containing little silica the test can be made in a few hours.

The exact nature of the yellow crust of the *fumarole* has proved a puzzle to many an acute observer. The guides sometimes present visitors with fragments of the cellular lava covered with this crust as specimens of "sulphur" (sublimates of sulphur at Vesuvius are rare), and I know one case in which a lady packed some of these so-called "sulphur" specimens into a box containing a favourite silk dress, which was soon destroyed. These yellow crusts are highly *deliquescent* and *acid*; they are impregnated with acid chlorides and sulphates of iron, aluminium, calcium, sodium, &c. The Italian coarse grey paper in which the specimens were enveloped was so thoroughly impregnated with these acid salts that, after being thoroughly dried, it was quite incombustible.

It was to "perchloride of iron" that Prof. Scacchi at first felt inclined to attribute the *yellow colour* of these incrustations; but when he found that this colour resisted the action of water he hesitated; and after a considerable number of ingenious tests, he came to the conclusion that it was due to "a very complicated mixture of various substances." He did not succeed in establishing the precise nature of the yellow substance to which the crusts owe their colour (*Sull'incendio Vesuviano, &c.*, 1855).

I have found that the lava covered with this yellow incrustation when mixed with boiling water rendered the latter very acid, and that pure water extracted a large amount of saline matter: chlorides and sulphates of iron, aluminium, alkaline earths, and alkalies; substances due to the action of hot steam with hydrochloric and sulphurous acids (and probably hydrofluoric acid, as we shall see), on the constituents of the rock. The temperature at which this vapour issues is 120° to 200° C., and sometimes much higher (500° C. has been noted in some cases).

Treated with strong sulphuric acid in the manner above described the incrustations gave abundant evidence of *fluorine*. That the yellow sulphur colour was not entirely due to any basic chlorides or sulphates of iron was proved when I submitted the yellow substance to the action of hot hydrochloric acid. It appears largely due to a *silicate of peroxide of iron*, associated with more or less *fluosilicate*, and only partially attacked by acids.

A silicate of iron with very similar characters, except that it is hydrated and soluble in hydrochloric acid, is found in Mexico, and has been called Anthosiderite, from *Anthos*, a flower, because it is often seen in the form of flower-like incrustations. It is curious to note that Scacchi has also met with the yellow incrustations at Vesuvius in the form of flowery crystallisations (*fioritura*, as he calls them). My specimens showed in some cases minute radiating crystals, but nothing like flower petals or feathers.

The pulverised substance, after the action of hydrochloric acid, I found to be still of a light yellow tint, and examined under the microscope the grains of transparent felspar (ryacolite) were seen to be *stained*, like a yellow topaz, to the extent of a quarter to a half or more of their substance by the yellow compound. This shows, over again, how porous are the most solid rocks and even crystals! The incrustations have a strong odour of *fluosilicic gas*, and it was this odour that led me to seek for fluorine in them.

With regard to the metal *Vesbium*, after carefully reading the paper of Prof. Scacchi (*Atti. della R. Acad. Napoli*, viii., 10), I am almost convinced that he was dealing with *molybdenum* and *copper* (and probably minute quantities of other substances), in the green and yellow crusts which he examined on the ancient Vesuvian lava. Nevertheless, further research is requisite, and I hope to repeat his experiments on the incrustated lava still in my possession.

The manner in which I detected molybdenum in the yellow crusts from the *fumarole* found in the crater of Vesuvius in the Spring of 1879, is as follows:—

The finely pulverised lava and its incrustation is treated with hot *aqua regia*; the solution, slightly evaporated and without filtering, is neutralised by ammonia in slight excess; yellow sulphide of ammonium is added, and the mixture allowed to remain for some hours in a closed vessel. It is then rapidly filtered and the filtrate neutralised with hydrochloric acid in slight excess. The flask is closed immediately with a cork, and allowed to remain thus *for two days*. At the end of that time the brown sulphide of molybdenum will be found upon the precipitated sulphur. (The sulphide of molybdenum requires a long time to precipitate in an acid liquid, and more so when its quantity is small). The precipitate is collected on a platinum dish and roasted, to drive off the sulphur and convert the sulphide into molybdic acid.

Copper and *lead* are invariably present in small quantities in the incrustated cellular lava. The yellow crust also yields *ammonia*, and there are indications of many

other substances to which I may refer later. I find that the lava *after* being treated with a boiling solution of caustic soda, *gelatinises* with hydrochloric acid, and this character may, perhaps, enable us to distinguish between the lava of modern and of ancient volcanoes.

Laboratory of Analytical Chemistry,
Putney, London, S.W.

RESEARCHES ON TURACIN, AN ANIMAL PIGMENT CONTAINING COPPER.*

Part II.

By A. H. CHURCH, M.A., F.R.S.,
Professor of Chemistry in the Royal Academy of Arts, London.

This paper is in continuation of one read before the Society in May, 1869 (*Phil. Trans.*, clix, pp. 627—636). It contains an account of observations made by other investigators on turacin and on the occurrence of copper in animals; a table of the geographical distribution of the Touracos, and a list of the twenty-five known species; a chart of turacin spectra (for which the author is indebted to the kindness of Dr. MacMunn); and a further examination of the chemical characters and the composition of turacin. The more important positions established by the present inquiry are these:—

1. The constant occurrence in eighteen out of the twenty-five known species of *Musophagidæ*, of a definite organic pigment containing, as an essential constituent, about 7 per cent of copper.

2. The "turacin-bearers" comprise all the known species of the three genera, *Turacus*, *Gallirex*, and *Musophaga*, while from all the species of the three remaining genera of the family *Musophagidæ*, namely, *Corythæola*, *Schizorhis*, and *Gymnoschizorhis*, turacin is absent. Furthermore, the zoological arrangement of the genera constituting this family is in accord with that founded on the presence of turacin.

3. The spectrum of turacin in alkaline solution shows, besides the two dark absorption bands previously figured, a faint broad band on either side of line F, and extending from $\lambda 496$ to $\lambda 475$.

4. The spectrum of *isolated* turacin in ammoniacal solution shows, besides the three bands already named, a narrow fourth band, lying on the less-refrangible side of line D, and extending from $\lambda 605$ to $\lambda 589$. It probably arises from the presence of traces of the green alteration product of turacin formed during the preparation of that pigment in the isolated condition; an alteration product which is likely to prove identical with Krukenberg's turacoverdin.

5. Turacin in ammoniacal solution remains unchanged after the lapse of twenty-three years.

6. Turacin in the dry state, when suddenly and strongly heated, yields a volatile copper containing red derivative, which, though undissolved by weak ammonia-water, is not only soluble in, but may be crystallised from, ether.

7. Turacin in the dry state, when heated in a tube surrounded by the vapour of boiling mercury, becomes black, gives off no visible vapour, is rendered insoluble in alkaline liquids, and is so profoundly changed that it evolves no visible vapour when afterwards strongly heated.

8. The accurate analysis of turacin offers great difficulty. The percentage composition, as deduced from those determinations which seem most trustworthy, is—

Carbon	53·69
Hydrogen	4·60
Copper	7·01
Nitrogen	6·96
Oxygen	27·74

These numbers correspond closely with those demanded by the empirical formula $C_{82}H_{81}Cu_2N_9O_{32}$, although the author lays no stress upon this expression.

9. Turacin presents some analogies with hæmatin, and yields, by solution in oil of vitriol, a coloured derivative, turacoporphyrin. The spectra of this derivative, both in acid and alkaline solution, present striking resemblances to those of hæmatoporphyrin, the corresponding derivative of hæmatin. But copper is present in the derivative of turacin, while iron is absent from its supposed analogue, the derivative of hæmatin.

Abstract of a Paper read before the Royal Society.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To General A. De Courcy Scott, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, April 19th, 1892.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 186 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 186 samples examined, the whole were found to be clear, bright, and well filtered.

The satisfactory character of the water supply to the Metropolis, commented on in our previous report, continued to be maintained during the month of March, the figures indicative generally of the smallness of the proportion of organic matter present in the water being substantially identical, though just a trifle higher, than those afforded by the results of the previous month, as shown in the following Table, in respect to the water furnished by the several companies drawing their supply from the Thames:—

	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
January	12·4 : 20	0·052	0·158	0·204
February	8·3 : 20	0·039	0·137	0·151
March..	8·6 : 20	0·043	0·144	0·188

We cannot close this report without giving expression to our sense of the loss we have sustained by the premature death of our much valued colleague, Dr. Meymott Tidy, esteemed not only by ourselves, but by all with whom he was brought into relationship, alike for his great professional knowledge and experience, especially in regard to water analysis and supply, and for his bright, kindly disposition and high personal character.

We are, Sir,

Your obedient Servants,

William Crookes.
William Odling.

AN EPISODE IN THE HISTORY OF SCIENCE.

AN incident which has been recently brought to light is not uninstructive. Close upon half a century ago, Mr. J. J. Waterston submitted to the Royal Society a memoir on "The Physics of Media composed of Free and Perfectly Elastic Molecules in a State of Motion." In accordance with routine, it was submitted to experts supposed to be qualified to form a just estimate of its merits. One of these referees pronounced the opinion that "the paper is nothing but nonsense, unfit, even, for reading before the Society." Another expert, who was also one of the leading authorities of the day, and who had evidently given the memoir his best attention, announces that: "The original principle itself involves an assumption which seems to me very difficult to admit, and by no means a satisfactory basis for a mathematical theory, viz., that the elasticity of a medium is to be measured by supposing its molecules in vertical motion and making a succession of impacts against an elastic gravitating plane." In consequence, Waterston's memoir was indeed read, and a brief and somewhat perfunctory abstract was printed in the *Proceedings*, but since then it has lain practically unnoticed in the archives of the Society. An account of the paper appeared also in the "Report of the British Association" for 1851.

So matters remained. Other persons arrived at conclusions similar to those announced by Waterston, and in due time reaped the credit of so doing. But, at last, Lord Rayleigh, Secretary to the Royal Society, unearthed Waterston's memoir, and has been instrumental in securing its appearance in the *Philosophical Transactions*.

It must not be supposed that we are taking up here our parable either against the Royal Society as a body or against the men upon whose judgment it relied. Scientific bodies with a high and well-earned reputation have to be very cautious to what papers they give their *imprimatur*. The referees also could judge only according to their own lights, and may in turn demand to be judged accordingly.

Lord Rayleigh makes here two suggestions which may be of use for the future. He thinks that "highly speculative investigations, especially if by an unknown author, are best brought before the world through some other channel than a scientific society." He even intimates that a young author who feels himself capable of great things might do well, before attempting higher flights, to perform work of a more limited scope and more easy to be appreciated. Did not Charles Darwin pursue this plan when he produced his monographs on Coral Reefs and on the Cirripedia? and was thus enabled to pose before the world as a sound and sober-minded inquirer before he dazzled his contemporaries with the startling search-lights of the "Origin of Species."

Another lesson implied in Lord Rayleigh's introduction to Waterston's paper, is conveyed in the following remark:—"One circumstance which may have told unfavourably upon the reception of Waterston's paper is that he mentions no predecessors." A young or a comparatively unknown inquirer will always find it good policy, if possible, to put forward his results or his conclusions as a development of what has previously been done in the same direction. Such a step, if judiciously taken, will guarantee the innovator against contemptuous disregard, as well as against an intentional "conspiracy of silence."

The value of Waterston's paper is now, of course, mainly historical. The work which he began has since been taken up and carried out by others. It must be admitted that Waterston first introduced the conception that heat and temperature must be measured by *vis viva*. Thus he completed Bernouilli's explanation of pressure by showing the accordance of his hypothetical elastic medium with the law of Dalton and Gay-Lussac. In the second section of his paper, Waterston showed that "in mixed media the mean square molecular velocity is inversely proportional to the specific weight of the molecules." From this generalisation, the law of Avogadro, and that of Graham on diffusion, may, as Lord Rayleigh reminds us, be deduced at once.

The chemical views advanced in his paper, in the opinion of Professor McLeod, "shadow forth many of the ideas of modern chemistry, and it might have been the means of hastening their reception by chemists."

Waterston distinctly expresses the opinion that "a molecule in motion, without any face to restrain or qualify it, is in every respect to be considered as a free projectile. Allow such free projectiles to be endowed with perfect elasticity, and likewise extend the same property to the elementary parts of all bodies that they strike against, and we immediately introduce the principle of the conservation of *vis viva* to regulate the general effects of their fortuitous encounters." Here, surely, the author approached very close to our modern kinetic theory of gases.

RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

(Continued from p. 206).

WE dissolve in 10 to 20 parts of hot water crystalline oxalic acid to the extent of 1½ parts of the quantity of oxide existing in solution, and add a small portion of the hot solution strongly acidulated with nitric or hydrochloric acid, and extremely diluted at first (containing about one-half per cent of oxide). The oxides separate at once as a semi-fluid mass, which generally collects together in soft lumps. These must not be immediately pressed with the glass stirring-rod, but the operator must wait for a few minutes until the oxalates have passed into a solid state, when the masses are broken up and the liquid is stirred briskly, when the precipitate in general distributes itself in the liquid for the most part as a fine powder; a further portion of a hot and rather more concentrated solution is added, again proceeding as just directed, until the liquid contains a considerable quantity of a fine powder.

The residue of the hot acid solution containing about 3 per cent of oxides is then added at once, stirring vigorously. The very voluminous precipitate is washed by decantation, allowed to drain on a filter, dried at 100° until it begins to crumble, and then completely dried over an open flame. A previous extraction of moisture is not advisable, as the mass forms then too compact fragments. The ignition of the oxalates in large quantities may, without hesitation, be undertaken in an iron capsule with a flat bottom. This vessel must have been previously scoured with sand, dried, rubbed with olive oil, and then heated to incipient redness. The iron thus becomes coated with a firmly adhering layer of ferroso-ferric oxide, which does not exfoliate even on repeated use.

When igniting the oxalates the following precautions must be carefully observed:—If after the destruction of the oxalic acid and the combustion of the carbon the oxide does not form a quite fine powder, but contains solid fragments, it must be allowed to cool, then be ground up finely in a mortar and ignited anew. During ignition the mass is diligently turned over and over so that all parts of the powder which have assumed a red heat on the bottom of the capsule may be brought in contact with the air whilst at this temperature. Thus the oxides are obtained as a fine uniform powder of a dark chocolate-brown colour. An oxide containing particles which have retained a light colour is not fit for the subsequent operation.

* *Berichte der Deutsch. Chem. Gesell.*

For separating cerium and freeing the basic cerium precipitate as far as possible from lanthanum and didymium, the proportion of nitric acid prescribed by Auer is not quite sufficient (supposing acid of 1·40 spec. gravity is understood) if lanthanum and didymium are present in percentage here assumed. It is most satisfactory to ascertain the requisite quantity of nitric acid by some previous experiments with small quantities of oxide. To this end 30 grms. oxide are stirred up with 30 c.c. of water in a porcelain capsule to a uniform paste, and at first 60 grms. nitric acid are added of specific gravity 1·20. On stirring, the mixture becomes heated, and a part of the oxide, including much cerium, dissolves with a yellow colour and with an escape of gas. The capsule is then heated on the water-bath for an hour, stirring diligently and supplying the water lost by evaporation. At the end of this time all the undissolved oxide is opened up, and the dissolved cerium is separated again. If small clots appear they are crushed with the pestle. So much water is then added that the total weight of the mixture reaches 140 grms., and it is then heated for an hour on the water-bath, with frequent stirring. If the liquid is now of a rose colour and the precipitate of a yellowish white, the quantity of nitric acid is sufficient. If the precipitate, on the contrary, is of a brownish rose colour, the liquid is evaporated down to the volume which it had before the addition of the nitric acid, and there are cautiously added from time to time whilst heating small portions of nitric acid of specific gravity 1·20 from a weighed flask, until the precipitate, after dilution to a total weight of 140 grms. and heating, has assumed a white or yellowish white colour. If the liquid as it becomes clear on the surface has a yellow instead of a rose colour, too much nitric acid has been added, and cerium has again passed into solution. In this case the dissolved cerium may be entirely re-precipitated by heating with a little oxide ground up with water in a mortar. After the sample has stood for twelve hours, a few drops of the solution are filtered through a dry filter, and the absence of cerium is ascertained by the extremely sensitive reaction with hydrogen peroxide, indicated by Lecoq de Boisbaudran. The same reagent was previously used by W. N. Hartley for the recognition of cerium, though in a somewhat different manner. The clear filtrate is best mixed, first with solution of hydrogen peroxide, then with a little strongly diluted ammonia until a turbidity begins to appear, and is then heated. In presence of cerium the gelatinous precipitate has an intense orange-yellow colour, whilst salts of lanthanum and didymium give only a colourless or a pale rose-coloured precipitate.

For the separation of the cerium, 500 grms. of the tested oxides are stirred up to a uniform paste with 200 c.c. of water in a capacious semicircular porcelain dish, and nitric acid of specific gravity 1·20 is slowly added in the proportion already ascertained, with stirring. In general, from 1100 to 1350 grms. of such acid will be required. After the violent reaction is over, the dish is placed upon a water-bath, kept in gentle ebullition, and heated for several hours, stirring frequently and occasionally replacing the water which has evaporated, until all brownish particles of oxide have been converted into yellowish white masses. The mass is then allowed to stand for nine hours, mixed in a decantation glass with 2½ litres of cold water, and allowed to settle for twenty-four hours.

The rose-coloured solution (which contains not a trace of cerium if the operation has been properly conducted) is poured off as clear as possible, and the liquid, which is turbid from a small quantity of precipitate, is poured into another vessel. The latter liquid is then poured upon a dry filter, and the filtrate is returned and re-filtered until perfectly clear. The solution which was first decanted off is then passed through the same filter.

The precipitate is now stirred up with 2½ litre solution of ammonium nitrate containing 7 per cent of the salt, again allowed to subside, and the liquid decanted off is poured upon a fresh filter moistened with the solution of ammonium nitrate, and proceeding as above in case the filtrate is turbid. The clear filtrate containing ammonium nitrate is collected separately. The precipitate may then be washed a second time in the same manner, though this is generally not worth the trouble. The precipitate is best brought upon the filter last used and allowed to drain completely with cautious stirring, when almost the entire quantity may be removed from the filter as a tough clayey mass.

The precipitate, dried at 100°, is then worked up for the pure cerium double salt as directed in the former section.

This remarkable substance possesses very different properties, and in any case different compositions, according to its manner of preparation. If it was separated from a mixture of oxides very rich in cerium it is, as Auer found, soluble in pure water, and from this solution it may be again precipitated by dilute nitric acid or ammonium nitrate, whilst the oxide obtained from an oxide containing the proportion of cerium above supposed is quite insoluble in pure water. In general, the precipitate dries up to a yellowish white powder, but if so much nitric acid was used in its preparation that a little cerium was dissolved, it appears, when dry, as a transparent mass resembling amber.

It is probable that in this substance there are not merely different ceric sub-nitrates, but also cerous oxide. By the method described, and by repeatedly working up the cerium double salt, there were obtained 808 grms. earths absolutely free from cerium, consisting of about one-half lanthanic oxide along with oxides of the didymium components.

(To be continued).

APPARATUS FOR THE DELINEATION OF CURVED SURFACES, IN ILLUSTRATION OF THE PROPERTIES OF GASES, &c.

By MORRIS LOEB, Ph.D.

In attempting the graphic representation of the relations between the volume, temperature, and pressure of gases, or of other problems involving three variables, one is met by the difficulty of properly constructing the surfaces in question. Drawing isothermals, &c., as projected upon a single plane, gives a very imperfect idea of the actual proportions. For many years this method has been occasionally supplanted by the actual construction, in papier maché or plaster, of models bounded on one side by the surface in question, relief maps in other words. This plan suffers from several disadvantages. Aside from the notion of solid volume which is involuntarily entertained in beholding such a model, some of the surfaces are too complex to be well shown in this manner. Furthermore, the models are rather hard to make, expensive, and occupy a good deal of room.

I have obviated most of these difficulties by obtaining a set of glass plates, about 11 c.m. square and 7 m.m. thick, ruled in squares 7 m.m. wide. Placed one on top of the other, these form a block whose perpendicular edge may be taken for the third axis in a system of rectangular co-ordinates. Having drawn upon a sheet of paper the curves representing the relation between volume and pressure at successively 0°, 10°, 20°, 30°, &c., of temperature, I can trace them, with suitable grease-chalks, upon the successive glass plates. When these are superposed, the curves exhibit the proper relations in space and afford a very fair idea of the nature of the surface of which they are elements, without arousing any sensation of an included volume. Since the lines can always be erased and replaced by others, a set of twenty plates suffices for all purposes, and the surfaces can be produced at a moment's notice if the necessary sketches on paper are preserved. Besides being useful for illustrating lectures in molecular

physics, the plates can also be employed to advantage in the construction of crystallographic, geological, and other models.

Where the parallax, inevitable for glass plates, becomes annoying, it is possible to substitute wide-meshed cotton netting, stretched upon square frames of uniform thickness. The curves can be embroidered upon the net, as it were, with pieces of coloured thread; although it is not quite so easy to make the lines conform to the drawing, the general effect remains the same.—*Journal of the American Chemical Society*, xiii., No. 10.

NOTE ON A QUALITATIVE TEST FOR CHROMIUM.

By L. W. McCAY, D.Sc.

In most works on qualitative analysis it is directed that an insoluble chromate* or a mixture of ferric, aluminic, and chromic oxides be tested for chromium by fusing the chromate or mixture with sodium carbonate and nitrate, treating the fused mass with water, filtering, and adding acid to the yellow filtrate. This addition of acid is said to change the yellow colour of the filtrate to a reddish yellow—changing the neutral salt to an acid salt. This would, of course, be true were there after the fusion no reducing agent present in the melted mass. There is, however, formed during the fusion a considerable quantity of alkali nitrite which dissolves with the chromate and which, upon the addition of acid to the filtrate from the insoluble residue, splits up into a corresponding alkali salt and free nitrous acid. This nitrous acid is often present in such quantities as to almost immediately (especially when the liquid is heated) reduce all the chromic acid to chromic oxide, and occasion a greyish blue solution, *which can completely mislead the beginner*. I venture to call attention to this point, which I insist is of sufficient significance to warrant mention, at least in such a standard work as that of Fresenius. It is but proper to add that in the "Quantitative Analysis" of both Rose and Fresenius the reducing action of the nitrous acid is mentioned, but, in Rose, with what seems to me scarcely a sufficient amount of prominence.

DIFFERENCES IN THE DETERMINATION OF REVERTED PHOSPHORIC ACID BY THE OFFICIAL METHOD OF ANALYSIS.†

By CHARLES GIBSON.

(Concluded from p. 210).

Now, I am of the opinion that a critical examination of the ammonia citrate solutions of the majority of State and analytical chemists would reveal the fact that they are very close in composition to my solution A—in fact, slightly inclined to acidity, the fact of slight acidity in the solution affecting the insolubility of the aluminic phosphate not being generally known; while the chemists of the manufacturers, and perhaps a few others, being cognisant of this fact, have taken precautions to have their solutions incline to alkalinity rather than acidity. In some such way as this may we account for a considerable portion at least of the large difference in the amounts of available P_2O_5 found by Messrs. Stillwell and Gladding on the one hand, and the State chemists and myself on the other. The results obtained in these experiments, which are only a few out of many that I have made, warrant, I think, the following conclusions:—

(1). That the official method, as it stands at present, is incapable of giving results on which an equitable adjustment of values—especially of aluminic phosphates—can be made, and it is urgently and imperatively necessary that either such modifications be made in it as will assure accuracy in all instances and under all circumstances, or that it be abandoned in favour of some other that may be depended upon.

(2). That it is possible to make such modifications in it as will enable analysts to obtain uniform and concordant results.

(3). That these modifications, if made in the direction which I will suggest, would conduce to greater accuracy and uniformity of results in the analysis of calcium phosphates.

With the view of making the comparison with the alkaline citrate method as accurate as possible, the amounts of available P_2O_5 obtained by it in these experiments and here given were determined as pyro-magnesium phosphate, checks being made by duplicates determined volumetrically. The agreement between the pyro-magnesium and volumetric determinations was very close, never varying more than 0·07 per cent. I have largely used this method during the last seven or eight years, and I have found it much more satisfactory than any other. The results obtained by it are reliable and uniform. It does not require that nicety and delicacy of manipulation and adjustment of solution that the official and other methods require, and there is therefore less liability to error. It is more expeditious, the available being determined in one operation. The presence of organic matter does not impair the accuracy of the results either for total or available P_2O_5, and it is therefore unnecessary to destroy it. The results can be obtained either gravimetrically or volumetrically. The only drawback I find in the use of the method is that, in order to make sure of a complete precipitation of the ammonia magnesia phosphate, after adding magnesium mixture and vigorously agitating it, I find it necessary to let it stand over night. As a substitute for the present official method, if the Association decides to abandon it, I think it might go farther and fare worse; and in any case it ought to be made an alternate method.

The present official method has been clearly demonstrated to be defective, erroneous, deceiving, and the cause of great financial loss in one case at least; and this Association, with whom alone rests the responsibility, and to whom alone we must look for a remedy, will, I am sure, recognise the necessity, and make some immediate change that will not only restore confidence, but will conduce to uniformity and constancy of results, and insure accuracy and justice.

I am aware that capricious changes in official methods of analysis are to be deprecated, but in view of the facts here presented, I realise that this association must perforce take action in the premises. Therefore, with a full consideration of all the facts, and the conclusions fairly deducible from these experiments, and with a desire to aid the Association in solving the problem with which it is now brought face to face, firmly believing that the changes here advocated will be a full and complete remedy for the defects in the official method which have been brought to light, I most respectfully submit the following suggestions:—

(1). That instructions be given to add ammonia hydrate to the ammonia citrate solution, until a faint alkalinity is perceptible with red litmus paper.

(2). That the time of digesting be made one hour at 65° C.

(3). That Joulie's alkaline citrate method, with or without the modification of weighing as pyro-magnesium phosphate, be made an alternate method.

* "Fresenius's Qualitative Analyse," Vierzehnte Auflage, §138, 10. Under Chromic Oxide, however, §102, 8, he says that potassium chlorate serves the purpose better than the nitrate. No reason for this substitution is given.

† From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

NOTES ON IRON IN BONE-BLACK.*

By Dr. BRUNO TERNE.

The freshly-prepared bone-black of the market yields on an average from 0·1 to 0·3 per cent of iron in the form of metallic iron, originating principally from iron mixed with the bones gathered up by the junk dealers, another portion coming from the wear and tear of the bone crushers and mills, and a very little from the iron vessels used in burning the bones.

Having been in charge for the last fifteen years of one of the largest plants for manufacturing bone-black, I had never experienced any trouble with our product, on account of the iron, until several months ago, when one of our patrons complained of an excess of iron in our black, which, according to his investigation, had run up in one instance to one-half of one per cent.

This complaint was coupled with the assertion that an increase of 0·25 per cent of iron above the average would materially impair the process of refining sugar.

This charge coming from a source commanding serious consideration, caused us to look into this matter thoroughly, but an examination of the literature of sugar refining, covering a period commencing with 1872 (Wagner's *Jahresberichte*) up to date, failed to disclose a single case in corroboration of the above cited assertion.

The more I thought over the matter the more I became convinced that the complaint made against our black, that it impaired the work of refining sugar liquors, was merely a convenient pretext to shield some irregularities in the process of refining, which otherwise would have to be shouldered at home. We all know that organic acids will dissolve iron, but in refining sugars the liquors should be free from acids, or, at least, nearly made free by previous neutralisation; the traces of free organic acids must certainly all be absorbed by the 6 to 7 per cent of carbonate of lime contained in fresh bone-black. The fact that in discarded black the yield of carbonate of lime is reduced to 3 or 4 per cent, and the yield of iron considerably raised, demonstrates clearly that fresh black operates to free sugar liquors from iron as well as other impurities.

In order to ascertain what effect a solution acidified with organic acid would have on the iron in bone-black, I prepared two solutions of citric acid containing respectively 0·1 per cent and 0·25 per cent of free acid.

The acidity of these solutions is so great that no sugar liquor entering filters will ever approach it in acidity.

I selected a black which had given by analysis a yield of 0·5 per cent of iron, and made the following experiments:—

Grms.		c.c.			Per cent.
(*a*). 5	of black with	500	citric acid solution of..		0·1
(*b*). 10	,,	,,	,,	..	0·1
(*c*). 5	,,	,,	,,	..	0·25
(*d*). 10	,,	,,	,,	..	0·25

I exposed the four flasks on the top of a steam heater for twenty-four hours to a temperature of 150° to 160° F., after which I tested the still acid solution for iron with potassium sulphocyanide and potassium ferridcyanide, but no trace of iron could be found in the solution.

Not satisfied with this I kept the flask for eighteen hours on a steam bath at a temperature of 200° to 212° F.; the results of the two experiments were absolutely the same.

To operate on a sample of black large enough to place the result of the experiment beyond any doubt, I took 250 grms. of the same black, yielding ½ per cent of iron, and treated the same with two litres of citric acid solution containing 0 25 per cent free citric acid, for twenty-four hours on the steam bath at nearly 212° F.

At the end of this time the acidity of the solution had completely disappeared and the absolutely neutral solution showed not a trace of iron with the most sensitive reagents (potassium sulphocyanide and potassium ferridcyanide).

I went still a step further and prepared a solution of iron in citric acid, 200 c.c. of which contained 1·01 grms. of iron; I took 100 c.c. and diluted to 500 c.c.; I mixed the dark yellow solution in a flask with 500 grms. of fresh regular sugar-house black, boiled up for thirty minutes, filtered, and obtained a perfectly limpid solution which contained not a trace of iron.

This experiment proved to my own satisfaction that an accidental excess of 0·25 per cent of iron in fresh black could not be charged with creating irregularities in the process of refining sugar liquors. But not being an expert in sugar refining I submitted this problem with the above results of my own researches to my friend, Dr. Arno Behr, now Secretary and Treasurer of the Chicago Sugar Refining Company, an acknowledged expert in this branch of chemical industry at home and abroad. I submit herewith an abstract of his letter:—

Chicago, Jan. 4, 1892.

My Dear Dr. Terne,— . . . "Iron is a very objectionable substance to have in filtered sugar solutions, because the refined soft sugars which are produced from such solutions take on a more or less gray appearance, which reduces their value considerably compared with others which are free from iron and of a bright yellow color.

"Colonial raw sugars contain sometimes a considerable amount of iron, and in the absence of good chemical methods for the removal of this iron from the unfiltered liquor, the refiner relies on the bone-black to absorb it.

"In some refineries the sugar solutions enter the black practically neutral, in others they are left a little acid, but this is of no conseqence, for you have found yourself that new black will absorb the iron even from a strongly acid solution. Even old working bone-black contains enough carbonate of lime (three to four per cent) to neutralise any considerable excess of acid. There is, however, a considerable difference in the behaviour of new and old black. Say you want to filter 100 pounds of dry sugar over 100 pounds of bone-black. Say this sugar contains two or three-hundredths of one per cent of Fe_2O_3. The solution will come from the new black absolutely free from iron, while from the old black half of it perhaps will be free, and the other half will contain it in increasing quantities.

"This will happen with properly neutralised liquor and without any fermentation having occurred. Even if the sugar solution enters the black free from iron, towards the end it will come from the old black containing iron.

"It works this way without any attempt having been made to wash the liquor out of the black. As soon as that is done matters become worse. Even from very good black the diluted sugar solution carries away a certain amount of iron.

"Now, in working it is found that the amount of iron increases in the black with its age, and that in the same proportion the amount of iron increases in the liquor. There is no way of removing the iron once absorbed by the black.

"There are three sources of iron in the black:—

(1). "The iron originally contained in the black.
(2). The iron in the raw sugar.
(3). "The iron taken up by the liquors and the bone-black in the sugar refining.

"The liquor has very little chance to dissolve iron, but the bone-black gets more or less of it by its passages through the kilns. The iron in the raw sugar the refiner has to take and make the best of, but in the case of the iron in the new black he will naturally fall back on the bone-black manufacturer and I do not blame him.

"It is reasonable to expect that a black with 0·1 per cent Fe will furnish iron-free liquors for a longer time than one with 0·3 per cent Fe. Most of the iron in new

* From the *Journal of the Franklin Institute*, April, 1892.

bone-black is in the metallic state and can be removed by running the crushed black over a magnetic separator.

"With best regards,

"Yours very truly,

"ARNO BEHR."

Certainly every one will agree with my friend Dr. Behr that 0·1 per cent impurity of anything is to be preferred to 0·3 per cent; the self-interest of the manufacturer will command the adoption of such means as to keep the percentage of iron as low as possible.

In the interest of manufacturers of bone-black everywhere, I thought it, however, of sufficient importance to refute the theory that an accidental excess of a fraction of a per cent over the acknowledged unavoidable proportion of iron in new black could be held accountable for any disturbance in the process of sugar refining, and to have my protest recorded with the section against such a claim.

This point has been fairly covered by my own experiments, and is clearly corroborated by the opinion of one of the most competent sugar chemists of this country.

Regarding the chemical methods of iron determination which are far too laborious to perform every day, I have been trying to find a method which could be carried on with sufficient accuracy without requiring previous chemical training.

I found that a boy, with the help of a magnet, could, by exercising the necessary care, make a determination sufficiently accurate for the daily control of a bone-black mill.

Take 100 grms. of the black and spread it in a thin layer over a sheet of white paper, then plough through it with a good magnet (I am using a six-inch horseshoe) and it will be found that most of the iron will be picked up at the first few passes.

After repeating the passes of the magnet in every direction, carefully observing that no part of the mass is missed, in a very few minutes all the iron will have been gathered upon the watch-glass ready for weighing. The results thus obtained come sufficiently close to those obtained by chemical test to serve as a control upon the process of manufacture, as the following examples will show.

The following tests have all been made within the last four months:—

	By Chemical Analysis. Per cent Iron.	By Magnetic Test. Per cent Iron.
October, 1891	0·360	0·410
„ 1891	0·160	0·219
December, 1891	0·387	0·501
January, 1892	0·100	0·130
„ 1892	0·169	0·213
„ 1892	0·080	0·107
„ 1892	0·199	0·224

While the magnetic test is invariably too high, it is sufficiently close to control the work of the black mills. The adherence of particles of carbon to the iron fully explains this result.

Regarding the chemical determination of iron, I consider a previous incineration of the black necessary, because there is a possibility that traces of organic matter left in the fresh black may be mistaken for iron by the reduction of the potassium permanganate.

Study of the Ammonium Chromates in order to obtain Ammonium Protoxide (or Trihydrazine, &c.), H_3NO.—E. Maumené.—The author refers to and continues certain researches of Vauquelin, Mohr, and Richter, concerning the neutral ammonium chromate. He hopes to continue these studies, and obtain a simple method of obtaining H_2N.—*Bulletin de la Soc. Chimique de Paris*, No. 6, 1892.

THE CHEMICAL ANALYSIS OF ALUMINUM.*

By ALFRED E. HUNT, G. H. CLAPP, and J. O. HANDY.

THE principal impurities found by us in commercial aluminum have been silicon, iron, and copper.

The present system of valuation of aluminum is based, chiefly, on the *total percentage* of *impurities*, but account is also taken of their *nature* and *relative amounts*.

Solubility of Aluminum.

Hydrochloric acid (sp. gr. 1·2) dissolves aluminum, in the form of drillings or chips, with very great rapidity. Sudden foaming up takes place, and much heat is produced. As this foaming often causes overflow, it is desirable to use a more dilute acid for analytical work. A mixture of 35 per cent hydrochloric acid (sp. gr. 1·2) and 65 per cent of water is better suited for general work.

Nitric acid (sp. gr. 1·42) when cold appears to have no action on aluminum. In boiling acid, however, the metal is very slowly dissolved.

Nitric acid (sp. gr. 1·2), similarly, has little or no action when cold. At the boiling point it dissolves aluminum slowly.

Sulphuric acid (sp. gr. 1·84), acting on aluminum, in the cold, soon forms on its surface a coating of sulphate, which protects the remaining metal. When heated, concentrated sulphuric acid dissolves aluminum slowly.

Dilute sulphuric acid, containing 25 to 50 per cent of concentrated acid, dissolves aluminum, in the cold, but only after a long time. Heating hastens the solution to such an extent that we have hopes of using this method of attack in determining iron hereafter.

Aqua regia, even that which contains only one-sixth as much hydrochloric acid as nitric acid, and a volume of water equal to that of the mixed acids, dissolves aluminum *almost completely* without warming and *fully* when heat is applied.

Potassium hydrate solutions of various strengths dissolve aluminum readily.

F. Regelsberger (*Zeit. fur angewandte Chemie*, June, 1891) uses potassium hydrate, usually in 40 per cent solution, as a solvent in the processes by which he analyses aluminum. 1 grm. of aluminum requires for solution about 15 c.c. of the 40 per cent KOH.

We do not favour this solvent for general work. Its use prolongs the analysis and renders close attention a necessity. The fatal objection, however, to its use in a laboratory where large numbers of aluminum analyses are to be made is its expense. It would cost three times as much as the acid processes which we employ,

Silicon.

a. Properties of Silicon in Aluminum.—In planning a method for determination of silicon in aluminum it is necessary to remember that it exists therein in two forms, the graphitoidal or crystalline and the combined form.

Properties of Graphitoidal Silicon.

When commercial aluminum is dissolved in any acid or mixture of acids, graphitoidal silicon remains behind, mixed with more or less silica. Our experiments show that this graphitoidal silicon has the following properties:—

a. It is oxidisable only to a slight extent by heating over a Bunsen burner or blast lamp. Oxidation proceeds slowly, even if the mass is frequently stirred.

We found that 0·1114 grm. of a mixture of silicon with a very small amount of silica gained 0·0050 grm. in one hour over a Bunsen flame.

In a second experiment, 0·0908 grm. of a mixture of silicon and silica (half and half) gained 0·0018 grm. in fifteen minutes, heating over a blast lamp.

* *Journal of Analytical and Applied Chemistry*, vi., No. 1.

TABLE I.

Separation of Silica from Silicon by Sulphuric and HF Treatment.

	No. 491. Grm.	No. 483. Grm.	No. 499. Grm.	No. 602. Grm.	No. 475. Grm.	No. 475. Grm.	No. 475. Grm.
Original weight silicon and silica	0·0218	0·0341	0·0183	0·0132	0·0909	0·0908	0·0297
Loss of weight by first HF treatment	0·0029	0·0136	0·0051	0·0041	0·0453	0·0460	0·0147
„ of first residue by HF treatment..	0·0039	0·0067	0·0020	0·0004	0·0094	0·0167	0·0061
„ of second residue by HF treatment		0·0057	0·0021	0·0009	0·0097	0·0098	

Oxidation by heating alone is therefore too slow to be of use analytically.

b. Graphitoidal silicon is gradually oxidised and dissolved by heating with 40 per cent potassium hydrate solution.

c. Fusion with sodium or potassium carbonate or nitrate quickly oxidises graphitoidal silicon and produces the corresponding silicate.

d. Notwithstanding the difficulty of oxidising graphitoidal silicon *completely* by heating it in the air, its *partial* oxidation by this means is sufficient to interfere seriously with any method which depends for success on its permanency, even for a short time.

Thus, when at the end of the first step in the determination of total silicon we obtain a mixture of silicon and silica, it would seem to be a very simple procedure to treat this weighed mixture with a few drops of sulphuric acid and 3 to 5 c.c. of hydrofluoric acid, evaporate, ignite, and weigh the *residual silicon*.

Unfortunately, as the experiments show, the determinations are not so simple. Of course, all the silica which was originally present has been volatilised by the hydrofluoric treatment, but we have left a *residue of silicon and silica* from the oxidation of a part of the original graphitoidal silicon. Having thus discovered that part of the graphitoidal silicon has been oxidised, we are left in doubt whether some silica from that source also has not been volatilised by the hydrofluoric acid treatment. Our experiments show that it has.

Thus, the apparent loss of weight by the HF treatment is made up of silica (originally present), plus silica from oxidation of graphitoidal silicon, and minus oxygen taken up by graphitoidal silicon. Table I. gives the results of experiments by this method, *first* on the original mixture of silicon and silica, and *then* on the residues from the H_2SO_4+HF treatment of the mixtures.

Thinking that better results might be obtained by washing the silicon out of the mixture by the use of dilute hydrofluoric acid alone, a few experiments were made. The weighed mixture of silicon and silica in a platinum crucible was stirred with 5 c.c. of Baker and Adamson's C.P. hydrofluoric acid, till lumps were disintegrated. Two parts of water were then added, and the mixture filtered. One wash was given with a mixture of 30 per cent hydrofluoric acid and 70 per cent water, and then a number of washings with water sufficient to remove the acid. The filter paper was then burned off and the residue weighed. Repetition of the washing, &c., showed that the graphitoidal silicon had been oxidised to a slight extent during the short heating required to burn off the filter paper.

TABLE II.

Separation of Silica from Silicon by HF Wash.

	No. 419. Grm.	No. 427. Grm.	No. 443. Grm.
Original weight of silica and silicon	0·0454	0·0561	0·0492
Loss of weight by first HF wash	0·0094	0·0123	0·0120
Loss of weight of residue from first treatment by second HF wash	0·0027	0·0018	0·0011

It is probable that the oxidation of the residual graphitoidal silicon can be wholly avoided by drying it on a weighed filter instead of attempting to burn off the filter paper, but we found that this would be impracticable for general work, because of the difficulty of weighing a number of filters under exactly the same conditions before and after HF washing.

We are now preparing to test for a method of filtration of the silica and graphitoidal silicon upon a platinum filter made in the form of a truncated cone, which will fit closely in the base of a platinum Gooch filter, or in such a filter without the perforated base. The scheme being to weigh the filter after washing the silica and silicon mixture with hot dilute hydrochloric acid and water, and finally with hot water and drying at 80° C., treating with hydrofluoric acid and sulphuric acid to dissolve the silica. Wash with hot water and weigh again without delay after drying at 80° C., the loss in weight being the silica in the mixture, and the residue being the graphitoidal silicon. This method bids fair to prove approximately accurate. The platinum truncated cone is being made as an enclosed box of platinum sheet soldered around a mass of an alloy of platinum and zinc, the top and bottom surfaces being perforated with fine holes for the passage of the liquids through it, the zinc being dissolved out of the alloy with sulphuric acid, leaving the interior of the cone a mass of platinum sponge to act as a filter. The filter can be cleaned from the graphitoidal silicon by immersing it in a mass of molten sodium carbonate in a platinum crucible, which will transform the silicon into silica, in which condition it can be washed out with hydrofluoric acid.

Combined Silicon.

A portion of the silicon in aluminum exists in the combined form.

The ratio of combined to graphitoidal silicon is, according to our experience, less the more silicon the metal contains.

Determination of Total Silicon.

0·9334 grm. of thin turnings or drillings are placed in a 4-inch evaporating dish. 15 c.c. of nitric acid (specific gravity 1·2), and 2 c.c. of concentrated hydrochloric acid are added and mixed, and the dish covered with a glass.

Solution takes place when evolution of NO_2 (hyponitric) fumes, showing that the conditions favour oxidation of combined silicon. In a few minutes, when action has nearly ceased, about 2 c.c. more of concentrated hydrochloric acid are added. This completes the decomposition of all except the very pure grades of aluminum. These require warming with the acid mixture for a time.

After the aluminum has dissolved, 20 c.c. of concentrated sulphuric acid are stirred in and the mixture evaporated quickly, on a hot plate, till it gives off fumes of sulphuric anhydride. The dish is removed before the aluminum sulphate separates and spirts.

After allowing it to cool for a few minutes, 75 c.c. of water and 10 c.c. of hydrochloric acid are added to the contents of the dish, and the whole well stirred. After boiling up for about five minutes, filter off the mixture of silicon and silica and wash with water, next with hot hydrochloric (30 per cent) acid, and finally with water till free from acid.

The filter paper is then burned off and the residue fused with about 3 grms. of sodium carbonate or fusion mixture. Cool the crucible containing the fusion by placing it in 25 c.c. of water in a 4-inch evaporating dish. Cover the dish, and add sufficient concentrated hydrochloric acid to decompose the fusion; when effervescence ceases, rub, and wash silica off from surfaces of crucible and cover, and remove the latter from the dish.

Add 15 c.c. concentrated sulphuric acid, and boil down the mixture to sulphuric fumes, on the hot plate.

After cooling sufficiently, add 75 c.c. of water and 10 c.c. of concentrated hydrochloric acid, boil up and filter. Wash thoroughly with water, 30 per cent hydrochloric acid, and finally water. Burn off, and weigh silica. As 0·9334 grm. of aluminum were taken for analysis, the weight of silica in grms. less the silica obtained from the fusion mixture divided by 0·02 equals per cent of silicon (total). We have many times treated with HF silica thus obtained and have always found it pure.

Our reasons for using sulphuric acid to dehydrate the silica are its rapid action compared with evaporation to dryness, and its leaving the silica in a form which filters easily. Evaporation of hydrochloric and nitric acid solutions to dryness fails to fulfil these requirements.

Determination of Iron and Copper.

1 grm. of aluminum is dissolved in 40 c.c. of a mixture of 33 per cent concentrated hydrochloric acid with 67 per cent water. When solution has been effected, boil up, dilute with warm water to 250 c.c., and pass sulphuretted hydrogen into the solution till saturated.

Filter off silicon, sulphide of copper, &c. The copper is separated from the residue and determined by any of the well-known methods. For instance, having obtained the copper in nitric acid solution from the ignited residue in which the silica has been rendered insoluble, the latter solution can be evaporated to dryness, and after ignition the residue of cupric oxide weighed. The copper may also be determined by battery precipitation from a dilute sulphuric acid solution.

The iron in the filtrate, from the precipitation with H_2S, is estimated by titration (after boiling down the solution to 50 c c.) by means of standard potassium bichromate. We use stannous chloride to reduce the Fe_2Cl_6, and mercuric chloride to take up the small excess of stannous chloride.

The metallic aluminum is usually obtained by difference in our commercial work, as we find that commercial metal made by electrolysis of alumina dissolved in molten fluoride salts very rarely contains any solid impurities other than silicon, iron, and copper. In some cases we have found sodium or potassium present, which we have separated and determined as in well-known methods of analysis for the alkalies in fire clays.

Determination of Aluminum.

The determination of aluminum in the commercial metal by difference is only approximate, for not only may there be alkali metals, but considerable amounts of occluded gases present to cause erroneous results, as well as the errors in determining the amounts of silicon, copper, and iron present.

In all important work we determine the percentage of metallic aluminum gravimetrically by precipitation, with hyposulphite of soda. The details of the method are as follows:—

1 grm. of aluminum is dissolved in about 25 c.c. HCl (35 per cent strong acid), and evaporated to dryness. It is then re-dissolved in dilute HCl by boiling, and is filtered from silica and silicon. The filtrate is diluted, warmed, and saturated with H_2S. CuS is filtered off and washed with H_2S water. The filtrate is boiled till free from H_2S, and made up to 250 c.c.; 50 c.c. of this solution are nearly neutralised with NH_4OH. Then 5 c.c. of saturated ammonium phosphate and 10 c.c. saturated sodium hyposulphite are added and the solution boiled till free from SO_2.

Filter and wash with hot water. Re-dissolve the $AlPO_4$ in dilute HCl, re-precipitate with slight excess of ammonia and a little phosphate, and boil.

Filter, wash, ignite in porcelain, and weigh as $AlPO_4$ containing 22·36 per cent aluminum.

Titanium and Chromium Alloys.

Titanium and chromium are added to aluminum to give hardness and resilience to the metal. Chromium gives the best results for hardness in castings. Titanium imparts more toughness and resilience, and is added when the metal is to be worked after being cast.

(To be continued.)

OBITUARY.

THE LATE GEORGE HOGARTH MAKINS.

George Hogarth Makins was born in 1815. He was educated for the medical profession, and passed the usual qualifying examinations, but he never practised. His tastes were from the first strongly directed towards chemistry, which he had the advantage of studying under Prof. Daniell, of King's College. After qualifying as a medical practitioner, he was successively lecturer on chemistry at the Aldersgate School of Medicine, and at the School of Middlesex Hospital. For a few years, 1849—1852, he carried on the manufacture of pure chemicals at Surbiton, and during this time prepared, by a process of his own, a considerable amount of spongy gold for the use of dentists. At the recommendation of Mr. Field, Assayer to the Mint, he then came to London, and after a preliminary study in the laboratory at the Mint, opened an assay laboratory in Coleman Street. This work proved a great success. He was soon appointed Assayer to the Bank of England, and afterwards made their referee. Mr. Makins introduced a number of improvements into the process of assaying. He designed a new balance which was described at the Chemical Society in 1852; he gave up the use of "trial plates," substituting for them pure gold and silver; he improved the apparatus employed for "acid parting"; he abolished the charcoal furnace, and substituted anthracite as the fuel. In 1863, Mr. Makins was obliged by ill-health to retire from the assay laboratory; he continued to give a short annual course on metallurgy at the Dental Hospital in Leicester Square till 1880. These lectures were enlarged and republished as a "Manual of Metallurgy" in 1862; a second edition, much increased in size, was brought out in 1873. Mr. Makins was elected a Fellow of the Chemical Society in 1845, and served repeatedly on the Council. He was an original Fellow of the Institute of Chemistry, and was a member of the Council at the time of his death.

Chemistry by no means absorbed the whole of Mr. Makins' energy; he was an amateur architect of considerable experience, and a thorough musician. He was devoted to the organ, and constructed himself three organs in the course of his life. Later in his life a new sphere of activity was opened to him. He was elected in 1880 to the Court of Assistants of the Society of Apothecaries, and for twelve years was most assiduous in his endeavours to promote the welfare of the Society. He became Master in 1889.

Mr. Makins retained his activity till a few months before his death, which took place on April 12, 1892. Mr. Makins was much esteemed by those who knew him. He was methodical and painstaking in his work, and of a very kindly disposition.

"Chemistry a French Science."—"History of Chemistry,"—so-called,—compiled by M. Jagnaux, and ably, though severely, reviewed in the *Chemiker Zeitung*, is avowedly written to demonstrate the dictum quoted above.

Action of Metals upon Salts dissolved in Organic Liquids.—Raoul Varet.—Certain metals capable of precipitating others from their salts dissolved in water lose this property if we substitute for water certain organic liquids.—*Bull. de la Soc. Chim. de Paris*, No. 6, 1892.

CORRESPONDENCE.

ON THE PREVENTION OF BUMPING.

When the presence of a heavy precipitate occasions bumping it is only requisite to keep it in suspension by mechanical means or by rapid ebullition to stop the bumping. Excluding cases of this kind bumping may take place in *homogeneous* liquids of alkaline, acid, or neutral reaction, and is due to the practical absence of air or gas from the liquid. Again, bumping takes place when *non-homogeneous* or immiscible liquids are attempted to be boiled or distilled together. However diverse these classes may appear, the ultimate cause of the bumping, I believe, is identical; so that preventive means ought to be equally efficacious in homogeneous or non-homogeneous liquids.

The only rational method for preventing bumping is to aërate the liquid; but the usual method of effecting this by bubbling air or gas through the bumping liquid is only of occasional benefit, and often worse than useless. Aëration, with its consequent prevention of bumping, is best accomplished by the slow and minute evolution of some insoluble gas in the liquid under operation. This can be elegantly accomplished in all cases where the liquid is an electrolyte by passing a current of electricity through it. The battery wires, which terminate in thin platinum wires, may be introduced inside a piece of glass tube, the end being fused, so that only the platinum wires (1 inch long) are in contact with the liquid.

The same slow and efficient aëration may be also accomplished by the introduction of some substance, best in fine powder, which will interact with the liquid and slowly evolve gas. For this purpose many metals may be employed, *e.g.*, zinc dust is widely applicable, evolving hydrogen in acid, alkaline, aqueous, and alcoholic solutions.

The addition of a minute quantity of zinc dust when estimating NH_3 by expulsion with NaHO, completely prevents all bumping. As in this case regard must be taken of the action of zinc on nitrate and nitrate-free NaHO used, so in all cases the secondary reactions must be carefully considered.

Methylated spirit, which can scarcely be used now without purification, distils quietly from all sorts of mixtures (as when recovering) on the addition of a little zinc dust.

Again, when it is attempted to distil mixtures of oil and water, or tar and liquor, recourse is generally had to heating and separating to get rid of as much liquor as possible before a troublesome distillation begins. However, by the simple addition of a grain or two of moistened zinc dust, mixtures of oil and water or liquor, in all proportions, may be distilled quietly in a flask of little more than double the capacity of the mixture taken. If necessary, the addition of zinc may be repeated, and if the solution is purely aqueous, a minute quantity of alkali may be added with benefit if permissible.

These examples will suffice to show how the principle may be employed in any case.—I am, &c.,

George Craig.

Lugar Iron Works, Cumnock, N.B.

DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILISERS.

To the Editor of the Chemical News.

Sir,—In reading the articles on "The Determination of Available Phosphoric Acid in Fertilisers containing Cotton-Seed Meal" (Chemical News, vol. lxv., pp. 163 and 170), I note that no mention is made of the probable formation of pyro-phosphates in the author's "incineration method." It is, I believe, generally acknowledged that the ash of organic manures is *not* available for the determination of phosphoric acid on this very account. I quote a few lines:—"It is believed that the disparity in all these cases is probably not so great as it should be; that is to say, that the incineration method as here used probably does not give the full content of phosphoric acid for this reason. The inferiority of the solvent power of nitric acid for phosphates to that of hydrochloric acid is well recognised. I believe that this inferiority is greater when the phosphate has been ignited."

I offer the formation of pyro-phosphates as a further and probably more serious source of error in the incineration method.

We have it on the authority of Fresenius that even fusion with alkaline carbonates fails to completely convert pyro-phosphates of the alkaline earths into ortho-phosphates with the exception of magnesic pyro-phosphate. I should myself incline to the direct solution in hydrochloric acid and potassium chlorate, but have no practical experience of cotton-seed meal fertilisers.—I am, &c.,

Wallis Jenkins, F.C.S.

5, Bishop Lane, Hull, May 3, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 15, April 11, 1892.

Researches on Persulphuric Acid and its Salts.—M. Berthelot.—Much of this paper is a reproduction of a memoir read by Mr. H. Marshall before the Chemical Society, and to be found in its *Transactions* for 1891.

The Decomposition of Silver Permanganate and a Peculiar Association of Oxygen with Silver Oxide.—Alex. Gorgeu.—The author's conclusion is that there exists between metallic oxides and oxygen a kind of association distinct from that known as occlusion, and in the state of combination properly so-called. The distinctive character of this association is to produce when broken up by the action of acids the separation of the whole or of a part of the oxygen over and above that of the protoxide in a form as inactive as that of the gas when in a free state.

On New Salts of Iron.—MM. Lachaud and C. Lepierre.—The bodies obtained are—

$(SO_4)_3Fe_2.SO_4Fe.4Am_2SO_4.3H_2O$, $(SO_4)_3Fe_2.3Am_2SO_4$, $(SO_4)_3Fe_2.SO_4Am_2$, $(SO_4)_3Fe_2$, Fe_2O_3.

These compounds have been obtained by melting a mol. of ammonium sulphate and a mol. H_2SO_4 to tranquil fusion (melting-point 121°), projecting into the liquid about one-fifth part of ferrous sulphate or of ammonium ferrous sulphate or even of iron-filings; the mixture is heated gently to expel the chief part of the water, and the application of heat is continued for a longer or shorter time according to the cases. Under these conditions several crystalline salts are formed in succession, for the most part insoluble in cold water, which, however, attacks them by degrees.

Researches on Certain Saccharine Principles.—J. Fogh.—A thermo-chemical paper, which does not admit of useful abstraction.

Action of Sulphuric Acid upon Certain Cyclic Hydrocarbides.—M. Maquenne.—Contrary to its usual manner of acting, sulphuric acid is capable of bringing certain cyclic carbides of the terpene family to the state of maximum hydrogenation. This hydrogenisation appears to be correlative with the escape of sulphurous

acid which always accompanies it. This is a further analogy between heptine and the true terpenes.

The Formation of Oxyhæmoglobine by means of Hæmatine and an Albumenoid Substance.—H. Bertin-Sans and J. Moitessier.—Under the conditions specified by the authors, hæmatine unites with the albumenoid matter of oxyhæmoglobine, forming at first methæmoglobine and then oxyhæmoglobine, unless, which does not appear probable, a mixture of hæmatine and of albumenoid matter could give the appearances and the complete series of spectral reactions which characterise hæmoglobine and its immediate derivatives.

Vol. cxiv., No. 16, April 19, 1892.

This issue does not contain any chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 6.

On the Solubility of Tricalcic Phosphate and Bicalcic Phosphate in Solutions of Phosphoric Acid.—H. Causse.—It appears from the author's researches that tricalcic phosphate dissolves in solutions of phosphoric acid in a much larger quantity than bicalcic phosphate. The cause of this difference seems to reside in an equilibrium which is established between three factors, water, phosphoric acid, and monocalcic phosphate. The water seems to play the principal part; it distributes its action between the monoclinic phosphate and the phosphoric acid, and everything depends on the proportion of these two compounds. The maximum quantity of dissolved phosphate corresponds to a solution containing 10 per cent of dissolved acid.

Cyanogen Compounds of Magnesium. — Raoul Varet.—The action of magnesium iodide upon mercury cyanide yields a compound of magnesium cyanide with mercury iodocyanide. The action of magnesium bromide upon mercury cyanide produces a compound of the same order.

On Metaphenyltoluene.—G. Perrier.—Already inserted.

Relation which Seems to Exist between Acid or Saline Solution, and the Molecular Weights of the Dissolved Substances.—Antoine de Saporta.—This paper does not admit of useful abridgment.

The Action of Carbon upon Alkaline Sulphates in Presence of Silica and of Carbon upon Sulphurous Acid. Application to the Production of Soluble Silica and of Glass.—Scheurer-Kestner.—The decomposition of the alkaline sulphates by silica and charcoal may be formulated according to the general equation:—

$$(SO_4R)+6(SiO_2)+5C=3S+4CO_2+CO+3(RO,2SiO_2),$$

the gases escaping consisting exclusively of free sulphur, carbon dioxide, and carbon monoxide.

Concentration of Sulphuric Acid in Apparatus composed of Cast-Iron and Platinum.—Scheurer-Kestner.—The author proposes the combination of two systems. The one consists in the use of a boiler of cast iron with a dome of platinum; the second in the employ of Kessler's well-known tanks, the first of platinum and the second of cast-iron. He has combined the two systems in one, composing an apparatus formed of platinum tanks, of Kessler's kind, preceding an apparatus with a cast-iron bottom. The greatest difficulty has been in joining the metals together. It has been overcome by the combined use of platinum, cast-iron, and lead connected with asbestos joints. Cast-iron is less attacked by acid at 95 per cent than by either stronger or weaker qualities.

The Colorimetric Determination of Iron. — J. Riban.—A controversial paper in reply to M. Lapicque (*Bull. Soc. Chimique*, ii., p. 295).

An Isomer of Chromium Sesquioxide.—A. Recoura.—Already noticed.

Journal fur Praktische Chemie.
New Series, Vol. xliv., Nos. 23 and 24.

The Action of Sulphurous Acid upon Isonitroso-Compounds.—M. Schmidt.—If the results obtained by the author's researches are briefly summarised it appears that in the isonitroso-compounds of the composition—

$$R_I—NOH$$
$$\quad\quad|$$
$$\quad H(R_I)$$

therefore alkyl derivatives of hydroxylamine sulphoxyl enter in place of hydroxyl, with the formation of substituted amidosulphonic acids. The compounds of the general formula $R_{II}—NOH$ may be arranged in three classes according to their behaviour with sulphurous acid. 1. Such as are very easily soluble in solution of sodium bisulphite, and form with it amidosulphonic acids so readily soluble that they do not separate from the solution or are readily oxidised, with the formation of brown masses, *e.g.*, nitrosophenol, nitrosoresorcine, &c. 2. Such which dissolve in solution of sodium bisulphite on boiling, and from the solutions of which, if decomposed with hydrochloric acid, amidosulphonic acid are separated. The formation of such compounds is accompanied by a reduction analogous to that which takes place on the conversion of quinone into hydroquinone. Of the three nitroso-naphthols only the two, α β, substituted are transformed by sulphurous acid in this manner, not the α-nitroso-α-naphthol. 3. Such isonitroso-compounds—$R_{II}.NOH$—can be distinguished which are not attacked by sodium bisulphite at all, *e.g.*, nitrosothymol, ethylnitrolic acid.

Communications from the Chemical Institute of the University of Kiel.—Th. Curtius and L. Pflug.—These comprise: "Preparation of Secondary Asymmetric Hydrazines by the Action of Aldehyds or Ketones upon Hydrazinhydrate," and "Substitution of Keto-Oxygen by the Azo-Group N_2," by Th. Curtius and Hans Lang.

Minor Communications from the Laboratory of E. von Meyer.—These comprise a memoir by P. S. Burns on the "Dimolecular Nitriles," a paper by H. Thiesing on "Methylendibenzamide and Analogous Compounds," and a note by H. Fleischauer on the "Condensation of Cyanides with Esters."

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. viii., No. 75.

Purification of Water.—Prof. A. R. Leeds.—From the Chemical News.

The Greenwood Process for the Direct Production of Chlorine and Caustic Soda.—From the Chemical News.

Fundamental Principles of the Chemical Analysis of Wines.—Prof. Fresenius and Herr Haas.—From the Chemical News.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Respiration of Plants and Animals.—In many books on Elementary Chemistry one finds it stated that animals exhale carbonic acid gas, and that trees and plants, &c, inhale it, retain the carbon and exhale the oxygen. In Sach's "Botany" it is stated very plainly that plants exhale carbonic acid gas in considerable quantity. Can you kindly recommend any book explaining this apparent contradiction?—I. L.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Industries," by Percy F. Frankland, F.R.S. (Cantor Lectures).
TUESDAY, 10th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "Photography in the Colours of Nature," by Frederick E. Ives.
WEDNESDAY, 11th.—Society of Arts, 8. "Uses and Applications of Aluminium," by G. L. Addenbrooke.
—— Geological, 8.
THURSDAY, 12th.—Royal, 4.30.
—— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
FRIDAY, 13th.—Royal Institution, 9. "The New Star in Auriga," by Dr. William Huggins, F.R.S.
—— Astronomical, 8.
—— Physical, 5. "An Instrument for Drawing Parabolas," by Richard Inwards, F.R.A.S. "Some Electrical Instruments," by F. H. Nalder. "An Instrument for Measuring Magnetic Fields," by E. Edser and H. Stanafield.
SATURDAY, 14th.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

TO CORRESPONDENTS.

H. S. L.—A simple chemical calculation will give you the information you ask for.

R. W. Tubb.—See a paper by Crace-Calvert and Johnson "On the Action of Sea Water on certain Metals in the CHEMICAL NEWS, vol. xi., p. 171.

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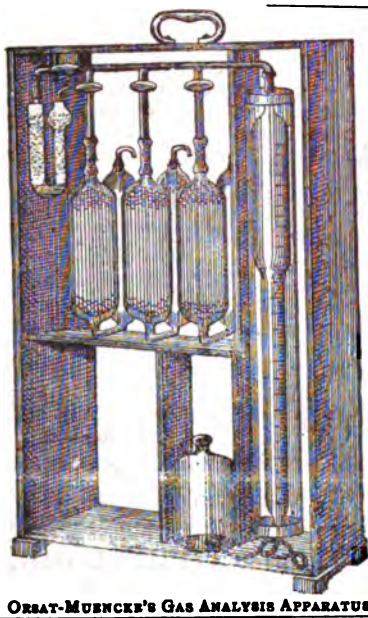

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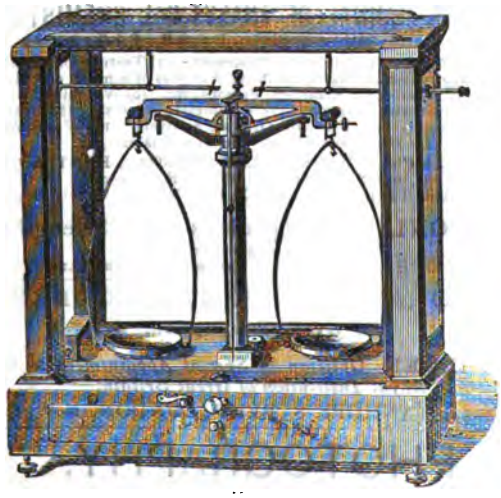

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THE CHEMICAL NEWS.

Vol. LXV., No. 1694.

REPORT ON PHOSPHORIC ACID.*

By W. B. BURNEY.

Adopting the usual method of reporting on phosphoric acid, the subject will be presented in the following order: (1) Condensed abstracts of methods published during the year; (2) results of work done by members of the association and others; (3) recommendations for the next year.

Abstracts.†

The Estimation of Phosphoric Acid by Ammonium Molybdate.‡

For the titration of phosphoric acid by molybdate, the latter should be acidified with three to four molecular proportions of nitric acid to one of molybdic acid, while the phosphate solution is only slightly acidified. Under these conditions one molecular proportion of phosphoric anhydride is exactly precipitated by twenty-four of MoO_3. Ten grms. of molybdic acid (or 12·262 grms. of crystallised hexammonium heptamolybdate) is dissolved in an excess of dilute ammonia, the solution neutralised, further acidified with 15 grms. nitric acid, and diluted to 1 litre. 24·3 to 24·5 c.c. precipitate 0·01 grm. P_2O_5.

For gravimetric determinations the author considers Finkener's method the best. The washed precipitate is dissolved in warm dilute ammonia, the solution evaporated until most of the ammonia is expelled, then mixed with an excess of nitric acid, evaporated, and heated to complete decomposition of the ammonium nitrate, the final temperature being about 180°. The residue contains 3·753 per cent P_2O_5.

If the precipitate has been washed with neutral ammonium nitrate, it may be titrated as follows:—It is stirred up with cold water containing phenolphthalein, and mixed with standard soda until it has completely dissolved and the liquid is red. It is then rapidly titrated back with nitric acid. One c.c. N/10 soda = 0·00061739 grm. P_2O_5.

Analysis of Concentrated Superphosphates.§

This superphosphate generally has from 4 to 5 per cent of P_2O_5 as ferric or aluminic phosphate, which is insoluble in water, but soluble in concentrated solutions of superphosphate. It is therefore important to use sufficient water in the first extraction, otherwise the soluble P_2O_5 will be reported too high. Take 1·5 grms. of the superphosphate, place in a beaker, and add a little water to soften and break up the lumps. Then make up to 90 c.c. Allow it to stand five minutes, and filter off the supernatant liquid. To the residue add 90 c.c. of water, stir, allow it to settle, and filter. Treat the residue with 60 c.c. of water, warm gently, bring upon the filter, and wash once with hot water.

Citrate Method, Phosphoric Acid Determination.‖

The author supposes that the double phosphates with ammonium form soluble compounds with ammonium citrate, and that only the magnesium ammonium phosphate is easily, but never completely, decomposed. To make this as complete as possible, more magnesium chloride than can combine with the ammonium citrate to form $MgNH_4C_6H_5O_7$ should be present so that this excess may act upon the compound—

$$MgNH_4PO_4+(NH_4)_3C_6H_5O_7,$$

which may have formed. Some $MgNH_4PO_4$, however, always remains in solution and causes a loss. When other bases (CaO, Fe_2O_3, Al_2O_3, MnO, FeO) are present, their phosphates are somewhat thrown down, and cause an error. With CaO the error is largest. If the lime has been removed by oxalate or sulphuric acid, a loss of P_2O_5 may always be expected if we do not use at least twice the amount of magnesia mixture usually prescribed. Silica always contaminates the precipitate when present. The author considers the molybdenum method more accurate.

In addition to the above article the author notes the following:*—

1. Treatment of the substance with hydrochloric acid is objectionable, as the precipitate may contain considerable silica.

2. Treatment with sulphuric acid reduces this error to about 1 m.grm. of silica.

3. Even when an excess of ammonium citrate is present and only little CaO, the precipitate contains from 1 to 2 m.grm. CaO as pyrophosphate.

4. The presence of manganese exerts a similar influence.

5. The error caused by Fe_2O_3 and Al_2O_3 in a sulphuric acid solution is very slight when little silica is present, even when large amounts of these oxides are present; they delay precipitation, however.

6. Small quantities of $Mg(OH)_2$ are always present; this error is slightest when the separation is made in a solution containing 2·5 per cent ammonia. In a nearly neutral solution, and in the presence of alkaline salts, the error is greatest.

7. The phosphoric acid is always incompletely precipitated.

8. In making a control analysis by the molybdate method, the method of treating substances rich in silica must be regarded.

The average error according to the author is ±0·128 per cent, the − result where only small quantities of P_2O_5 are present.

With Thomas slags and raw phosphates the results are always too high.

The Use of Phosphoric Acid of Animal or Mineral Origin in the Cultivation of the Sugar Beet.†

The results showed that no difference exists between the superphosphates of either animal or mineral origin.

Estimation of Phosphoric Acid in Slags. Formation of Tetrahydrated Ferric Phosphate.‡

In eliminating by means of nitric acid the residual hydrochloric acid from slag, which had been treated with the latter reagent to remove silica, a probable source of error is shown by the author in that a tetrahydrated ferric phosphate, $Fe_2(PO_4)_2+4H_2O$, is precipitated as a yellow granular powder. This differs from the normal ferric phosphate resulting from the precipitation of a ferric salt by disodium phosphate in not suffering dehydration at 110°.

Estimation of Phosphoric Acid in the Presence of Silica.§

The author proves by numerous experiments that phosphoric acid may be estimated in the presence of pretty large quantities of silica (solution of soluble glass acidified with hydrochloric acid was employed) when the precipitate of ammonium phosphomolybdate is washed with pure

---

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

† These abstracts were prepared by Mr. W. H. Krug, of the Chemical Division, Department of Agriculture.

‡ Hundeshagen, Fres., *Zeitsch. fur Anal. Chem.*, xxviii., 165—172.

§ Hughes, J., Chem. News, lx., 91.

‖ Reitmar, O., *Zeitsch. fur Angew. Chem.*, 1889, 702—9, and 1890, 19—25.

* Reitmar, O., *Zeitsch. fur Angew. Chem.*, xc., 196—210.

† Stoklasa, J., *Böhm. Zeitsch. fur Zuckerindustrie*, xiv., 137—142 *Chem. Centralbl.*, 1890, i, 771.

‡ Arth, G., *Bull. Soc. Chim.* (3), ii., 324—327; *Journ. Chem. Soc.*, March, 1890, 292.

§ Preis, K., *Listy Chem.*, xiii., 153, 154; *Journ. Chem. Soc.*, July, 1890, 825.

cold water. As the liquid runs through the filter turbid at the end, double filters should be used.

Results of Work Done During the Year.

In answer to a circular letter sent out in the spring, forty-four replies were received, and thirty-seven chemists consented to participate in the work on phosphoric acid. It is to be regretted that many of these have failed to analyse the samples sent them. Early in May three samples were sent to each chemist consenting to do the work, and consisted as follows:—

No. 1. A superphosphate.

No. 2. A complete fertiliser.

No. 3. A complete fertiliser containing cotton-seed meal and other substances difficult to oxidise.

These samples were prepared with the utmost care, and no pains were spared to insure absolute uniformity in the materials submitted for examination. The fertilisers had probably been made many months when they were collected for this work. They were first air-dried in thin layers for several days, and after grinding were passed through a sieve of forty meshes to the linear inch; the samples then stood for several days more, and were again mixed, first, in large jars, then by passing through a coarser sieve, and finally by hand on heavy paper, after which they were rapidly bottled and sealed.

From the specimens herewith submitted you may judge of the thoroughness of this work. It does not appear probable, therefore, that the differences in the analytical results presented in the following tables* can be attributed to any lack of uniformity in the samples, or to any dereliction on the part of your reporter.

These tables reveal discrepancies alike discouraging and inexplicable. It does not appear that we have made any advance since last year. That the methods employed in these determinations are trustworthy when properly executed follows from the fact that in the hands of a few experienced analysts the results are fairly within the limits of the working error. The fault, therefore, must be ascribed to the chemist, and is doubtless due to a lack of thoroughness, to a want of scrupulous attention to minute details in the processes of solution, precipitation, filtration, washing, &c. Thus we see results which seem to be too high through incomplete washing of the precipitate of ammonium magnesium phosphate; total phosphoric acid too low, owing to incomplete oxidation in the process of solution; insoluble phosphoric acid too high or too low, because the ammonium citrate solution was too strong or too weak, acid or alkaline, and so on.

Comment in detail upon the analytical data seems unnecessary. A very few words will suffice. In the first place the averages are given for what they are worth, and it is not claimed nor believed that in all cases they correctly represent the percentage of phosphoric acid present in the sample. The results on moisture are noteworthy, and seem to point to some grave oversight in the execution of the official method, if indeed the method was employed in all cases. It would be interesting to know how many of the chemists actually tested the steam closet to see that the temperature approximated 100° C.

With the possible exception of the soluble, the results on phosphoric acid cannot as yet be regarded as satisfactory. So long as experienced analysts differ, in extreme cases, by 0·7 to 0·8 per cent, and from the average or probable truth by 0·3 to 0·4 per cent, it must be admitted that there is room for improvement. Now if we omit from each table three or four of the analyses which seem to be extreme, there still remain a number which differ by the amounts above mentioned. Nor is this discrepancy confined to any one kind of phosphoric acid, but it is in varying degree true of all.

In the opinion of the reporter, the remedy for all this is to be sought not so much in the improvement of the methods of analysis, as in the increased care with which the details of the methods are executed after having been once adopted by this association.

Believing that changes in the official methods should be made with the greatest caution, and only for the best of reasons, the following recommendations are suggested after much hesitation:—

1. That in the preparation of the solution of water-soluble P_2O_5 the washing be continued until the filtrate measures 300 c.c.

2. That in *Chemical Bulletin*, No. 24, p. 225, the second line from top of page be changed to read as follows:—Filter the warm solution quickly through a 12½ centimetre plaited filter, wash twice with half-strength ammonium citrate solution, and then with water of ordinary temperature.

3. That in all cases of fertilisers containing cotton-seed meal, the solution for total phosphoric acid be prepared by the $Mg(NO_3)_2$ method.

4. That the association advise, in the preparation of the solution of total phosphoric acid, the use of method No. 2 (30 c.c. HNO_3+HCl) for superphosphates and other samples free from organic matter; and the $Mg(NO_3)_2$ method for all cases in which organic matter is present.

It is further recommended that with these changes the present methods of determining phosphoric acid be continued, subject, of course, to modification by the association.

[* The long Tables which follow are omitted as not being necessary or a comprehension of the processes and the arguments based thereon.—*Ed.* C. N.]

ON THE

ISOMORPHISM AND COMPOSITION OF THORIUM AND URANOUS SULPHATES.

I.—Chemical Discussion.

By W. F. HILLEBRAND.

During the course of an extended investigation on uraninite (*Bull. U.S. Geol. Survey*, lxxviii., 43, 1889—1890), it was often necessary to decompose the mineral in sealed tubes with sulphuric acid. At first a deposit was generally observed on removing the tubes from the oven, the character of which depended on the concentration of the acid and the presence or absence of thoria in the mineral. In the absence of this earth it took the form of a greenish powder with a strong acid, and of bright green, brilliantly reflecting crystals when a weak acid was used, unless the ratio of liquid to mineral was sufficiently high in the latter case to prevent crystallisation. As might naturally be supposed, these crystals were hydrated uranous sulphate. The best results as regards size of crystals were obtained with an acid containing 1 part of sulphuric acid to 5 or 6 of water by volume. With about 100 parts by weight of such an acid to 1 of the oxide UO_2, it might pretty confidently be expected that no crystallisation would take place.

In presence of thoria the green crystals still appeared, but they then contained thorium as well as uranium, and accompanying them was a beautiful, white, coherent, spongy mass, extending the length of the tube, and consisting of a network of microscopic needles grouped in radiating bunches. This was likewise a double sulphate of uranium and thorium, resembling in every respect the deposit formed under similar conditions from a solution of thorium sulphate alone, except that when washed, dried, and compacted together, there was a faint greenish tinge to it. Ordinarily the two forms of double salt appeared together, and it even seemed as if under favourable conditions, which have not yet been precisely determined, the crop of green crystals might be increased at the expense of the white deposit. At least, on one occasion, when the heating was prolonged for several days, the latter gradually disappeared, while the former increased in size and number. The white deposit always

preceded the green crystals, and by regulation of the proportions of oxide and of acid, and of duration of heating, it is possible in practice to obtain the former alone, if desired.

In order to secure material for exact chemical and crystallographical determinations, recourse was had to the artificially prepared oxides U_3O_8 and ThO_2, by using which, either alone or mixed in varying proportions, different products were obtained. Neither uraninite nor uranium dioxide, UO_2, is well adapted for this purpose, because of contamination of the crystals by sulphate of lead in the one case and by undissolved dioxide in the other. Even when using the oxide U_3O_8, care must be taken to avoid a like result by fine pulverisation and avoidance of excess of oxide as compared with acid. So slightly soluble are the green crystals that over 50 per cent of the dioxide UO_2 in uraninite, or in the oxide U_3O_8, can generally be obtained as sulphate. Hence it follows that when the dioxide is to be estimated volumetrically, care must be taken to use sufficient dilute acid to render impossible the formation of these crystals. The white, spongy deposit, is not a hindrance to the exact estimation of the dioxide by potassium permanganate, for it dissolves readily in cold water, though with extreme slowness when once it has been compressed.

The green crystals were separated from their mother-liquor in a Gooch crucible, without asbestos felt, with the aid of suction; they were at once washed with hot dilute sulphuric acid, then with alcohol, and finally with ether. They were allowed to dry thoroughly in the air and were analysed in that condition. It was found by experiment that alcohol was practically without solvent action on the sulphates, and that none of the water of crystallisation was removed by it. If both forms of deposition occurred at one time, the spongy one was first removed with great ease by two or three rapid washings with cold water—the network of fine needles being partly dissolved and partly carried through the holes in the crucible by the powerful suction—after which alcohol and ether were used as before. The results of analyses were as follows:

	I.	Molecular ratio.	II.	Molecular ratio.
UO_2	49·18	1·00	48·40	1·00
ThO_2	3·59	—	5·58	—
SO_3	32·08	2·05	31·27	1·96
H_2O	14·18	4·04	14·84	4·13
	99·03		100·09	

A sample of uraninite decomposed by dilute sulphuric acid in a tube at about 170° C. furnished the product whose analysis is given under I. An earlier and very similar analysis of another preparation may be found on page 50 of the Bulletin cited. The loss is mainly, if not altogether, undetermined lead oxide from included lead sulphate, which accounts in part for the excess of SO_2 found. For No. II. the oxides U_3O_8, ThO_2, were taken in such proportion that there should be about six times as much uranium dioxide as of thorium dioxide. Inasmuch as only 0·1622 grm. was available for sulphuric acid and water determinations in this analysis the ratio is not bad. One or two attempts to obtain a product with more thorium and less uranium by starting with correspondingly different proportions of the oxides ThO_2 and U_3O_8, were unsuccessful, perhaps because of the tendency of thorium sulphate to separate at once in the spongy state, and thus to reduce the amount available for slow crystallisation with the uranium. The specific gravity of No. II. was kindly determined by Mr. L. G. Eakins in alcohol of 0·7956 density. It was found to be 4·563 at 24·3° C., which, calculated for water at the same temperature as standard, becomes 3·63. The material examined contained 1·04 per cent of the oxide U_3O_8 undissolved, which does not appear in the analysis, and, allowing for this, a density of 7·3 (Clarke's tables), that of the double sulphate having the given composition is found to be 3·61 at 24·3° C.

The uranium sulphate, of which the analysis is here given, was obtained by decomposing the oxide U_3O_8 with dilute sulphuric acid in the manner already mentioned. Its density was not ascertained.

	II.	Molecular ratio.
UO_2	53·99	1·00
SO_3	31·94	2·00
H_2O	14·13	3·94
	100·06	

It appears, as was to be expected, that thorium is capable of replacing uranium in the sulphate of the latter which holds in combination four molecules of water. That this is a true case of isomorphism is most fully shown by Mr. W. H. Melville in the crystallographical part of this paper, although the habit of the uranium sulphate differs from that of the double salt.

While, as above stated, failure resulted from attempts to lower the ratio between thorium dioxide and uranium dioxide in the green double salt, it was found that the spongy mass, which almost always formed in the tubes when thoriferous uraninite was decomposed with dilute sulphuric acid, contained a very much higher proportion of thorium, and that by taking the dioxides in varying proportions, double salts of correspondingly different composition could readily be obtained, as is shown by the following analyses:—

	I.	Molecular ratio.	II.	Molecular ratio.
UO_2	34·34	1·00	16·92	1·00
ThO_2..	19·84		36·07	
SO_3	31·48	1·95	32·66	2·05
H_2O (diff.) . ..	14·34	3·95	14·35	4·01
	100·00		100·00	

Both salts were obtained from a mixture of the oxides U_3O_8 and ThO_2. In the case of No. II. the proportion was such that the uranium dioxide of the compound U_3O_8 was to the oxide ThO_2 as 2 to 1. It happened that the tube containing this preparation lay unopened for several weeks after removal from the oven, but during this time there had been no perceptible resolution of the precipitate, which on agitation made a thick emulsion with the acid. Both products were thrown on a Gooch crucible without asbestos felt, quickly washed twice or thrice with hot dilute sulphuric acid, and then with alcohol and ether, whereupon they were allowed to dry thoroughly in the air.

There is no reason to doubt the isomorphism of this salt with that formed under similar conditions from thorium alone, but whether these are crystallographically referable to the green crystals before described, or form a new case of dimorphism, must remain undetermined until the crystallographic features of the former are known. In polarised light, the needles of the double salt extinguish apparently parallel to their length.

Such contradictory statements appear in the literature of the subject regarding the composition of thorium sulphate separated from hot acid solutions—some authorities claiming 4½ mols. of water of crystallisation and others only 4—that it is very satisfactory to have evidence like that furnished by the above analyses to throw light upon the question. The tendency of late years has been to admit a mutual replaceability of thorium dioxide and uranium dioxide in chemical compounds, though no direct proof seems to have been heretofore established, and it was therefore reasonable to suppose that the composition of the thorium sulphate in question should correspond with that of the well-known uranous sulphate with 4 mols. of water. In the light of the above analyses there is no room to doubt the complete isomorphism of the two sulphates, and that Demarcay (*Comptes Rendus*, xcvi.

1860) and Roozeboom (*Zeit. Phys. Chemie*, v., 195) were right in accepting the formula $ThO_4(SO_2)_2.4H_2O$, derivable from the more or less incomplete analyses of Berzelius, Berlin, and Chydenius, in preference to $ThO_4(SO_2)_2.4\frac{1}{2}H_2O$, afforded by the more numerous ones of Delafontaine.*

In possible explanation of Delafontaine's high results for water, Roozeboom† very justly remarks that because of its physical character the salt retains much mother-liquor, and that if this be not removed at a temperature above 45° C., the $9H_2O$ salt is formed from it on cooling, so that it is almost impossible not to find too much water. Notwithstanding numerous attempts to prepare the salt $ThO_4(SO_2)_2.4H_2O$ from hot acid solutions as well as from warm neutral ones, I have never myself succeeded in reducing the water to 4 mols., even though the mass of needles was rapidly washed with hot dilute sulphuric acid and then with alcohol and ether, after freeing from mother-liquor by powerful suction on a Gooch crucible without asbestos felt, but my faith in the correctness of the formula with $4H_2O$ is not hereby shaken. A further possible cause of high results will appear from the following:—The air-dried salt is said by Delafontaine to be thoroughly non-hygroscopic, and for a given temperature and hygrometric condition of the atmosphere it is true that no change in weight does occur; but if the salt be weighed from day to day, or even twice a day, a very marked gain or loss of weight is observed, depending in degree on the amount of change in the atmospheric conditions. In August and September, when hygrometric and thermometric readings were often high, and marked and rapid changes were not infrequent, this gain or loss sometimes amounted within 24 hours to over 0·5 per cent of the total weight of the salt, and the extreme change during those months reached 1·22 per cent. It is therefore patent that the formula afforded by analysis may materially depend on whether the salt analysed was weighed when the weather was hot and moist or cold and dry.

It may not be out of place here to call attention to a possible cause of the frequent discrepancies noticed in the statements of different writers in regard to the amounts of water given off by different substances when placed over sulphuric acid in a desiccator. No one would deny that sulphuric acid of maximum concentration is superior as a drying agent to the same acid somewhat, if only slightly, diluted; but it is probably not known to every one how much may depend on the strength of the acid used. A case in point is the following:—A thorium sulphate containing, air-dried, 15·22 per cent H_2O, or 4·23 molecules, lost weight over concentrated sulphuric acid in a tightly-closed desiccator, as shown in column I. and as in column II. over acid, which had been in use in another desiccator for a considerable length of time, and was subsequently found to have a density of 1·66. The cases are not rigidly comparable, perhaps because of the different times devoted to the experiments, which were not carried on simultaneously, but they serve to illustrate the point.

This may be considered an extreme case, but it shows plainly the importance of using fresh acid of full strength whenever experiments of this kind are to be made, in order that results may be properly comparable.

Similarly it is improbable that a highly hydrated substance, which loses much of its water at 100° C., would show as great a loss when dried in an ordinary air-bath as in a current of dry air of that temperature.

I.		II.	
Time in days.	Acid of 1·84 sp. gr. Per cent.	Time in days.	Acid of 1·66 sp. gr. Per cent.
1	3·80	1	2·87
3	2·78	1	0·40
5	1·37	3	0·06
9	0·22	—	—
—	—	5	3·33
18	8·17		

Another point to be considered when it is desired to find the maximum amount of water that can be removed by any drying agent in a desiccator (which, of course, as a method, is in general inferior to that in which a continuous current of dry air or other gas is passed over the substance) is that, if many days are required for its removal—in other words, if the substance is slow to part with its moisture—the later weighings should not be made from day to day but at ever-increasing intervals, otherwise a prematurely constant weight or even an increase may be observed. This is due to the fact that whenever the desiccator is opened, which must be twice for each weighing, it, at least in the upper part, becomes filled with moist air, and the substance itself may absorb some moisture before it can be returned to the desiccator; one or more days may then be required to restore the condition of equilibrium which obtained between the vapour tensions of water in the salt and in the air of the desiccator prior to opening the latter. Especially if the acid has become somewhat weakened is it possible for an increase to take place.

Originality is not claimed for the above observations on methods of drying, but it seems as if attention could not be too strongly or too frequently drawn to the points mentioned, which there is reason to fear are not always observed.—*American Chemical Journal*, xiv., No. 1.

* *Ann. Chem.* (Liebig), cxxxi., 100. The statement by Kraut, near the foot of page 687 of "Gmelin-Kraut's Inorganic Chemistry," Vol. II., Part I., is manifestly unwarranted. He considers the evidence in favour of the $4H_2O$ salt as insufficient, and thinks the analyses affording this formula were made upon mixtures which might have resulted through absorption of water by the $3H_2O$ salt. It is strange that individuality should have been accorded by Chydenius and Oleve to this latter salt, which the former obtained by drying over sulphuric acid, after washing with hot water, the precipitate formed by boiling a weakly acid solution of the sulphate. Roozeboom is certainly correct in excluding this $3H_2O$ salt from the list of thorium sulphates.

† *Loc. cit.*, p. 202.

A COMMERCIAL METHOD FOR THE CONVERSION OF MINERAL ANTIMONITE INTO THE ORANGE COMPOUND.

By H. N. WARREN, Research Analyst.

As is well-known, the mineral sulphide of antimony has been frequently employed in the laboratory as a source for obtaining pure gaseous SH_2 by the action of hydrochloric acid upon that substance. By careful observations it will be found that the mineral substance is somewhat more soluble in hot hydrochloric acid than the orange compound; and by taking advantage of this property, the author has supplied a method for the conversion of that substance into the orange compound, adapting the same as a pigment. In arranging for this reaction hydrochloric acid is so diluted as to allow, when raised to the required temperature, an exact solution of the antimonite employed. The solution so formed should now, upon the addition of SH_2, precipitate the whole of the antimony as the orange sulphide; the acid thus set free being employed for a further use with a fresh addition of mineral.

The apparatus employed consists of a convenient sized retort, into which is introduced the required quantity of mineral along with its accompanying solvent, and heat is applied so as to maintain a steady evolution of gas.

To the retort is connected several suitable receptacles containing a quantity of already prepared solution of antimony chloride, and the issuing gas from the retort allowed to traverse the whole; the orange compound thus precipitated is filtered from its acid solution, washed and dried, and the filtrate so formed returned to the converter for continued action upon a further quantity of mineral.

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RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

Treatise I.

By P. SCHÖTTLANDER.

(Continued from p. 220).

3. *Separation of Lanthanum and Didymium by the Oxide Process.*

Under this name Auer von Welsbach describes a method of separation founded upon the formation of basic nitrates by the action of a mixture of the earths upon the neutral nitrate solution of the same mixture, and the much stronger basicity of lanthanum oxide as compared with the earths of the didymium and the yttrium group. In consequence of this stronger basicity lanthanum oxide remains predominantly in solution as a neutral nitrate, whilst the didymium and the still more feebly basic yttrium earths accumulate in the insoluble basic precipitate.

The basic precipitates obtained in this manner are essentially nothing else than hydrated compounds of the known basic didymium and lanthanum nitrates—

$$3Di_2O_3.2Di(NO_3)_3 \text{ and } 3La_2O_3.2La(NO_3)_3,$$

in which it is quite possible that in the first compound a part of the didymium may be replaced by lanthanum and inversely in the second a part of the lanthanum by didymium, which, in practice, does not come into consideration.

If we overlook this possibility the process may best be explained by a special case. If a solution contains equal molecular quantities of lanthanum and didymium we precipitate one half of the solution with oxalic acid, convert the oxalate into oxide, and treat this oxide, according to Auer's method, with the other half of the solution; the decomposition may then be represented by the following equation:—

$$\underbrace{6La_2O_3+6Di_2O_3}_{\text{Mixed Oxides.}}+\underbrace{12La(NO_3)_3+12Di(NO_3)_3}_{\text{Solution.}}=$$

$$=3\,[3Di_2O_3.2\underbrace{Di(NO_3)_3}_{\text{Precipitate.}}]+3La_2O_3.$$

$$\cdot 2La(NO_3)_3+\underbrace{16La(NO_3)_3}_{\text{Solution.}}$$

Then come first in reaction $3La_2O_3$ of the mixed oxide with $8Di(NO_3)_3$ of the solution, and form—

$$6La(NO_3)_3+3Di_2O_3.2Di(NO_3)_3,$$

upon which the residual oxides combine with corresponding quantities of the dissolved nitrates to form basic salts.

The results of numerous experiments (always approximately checked as regards the yield of oxides in the solution and the precipitate) always agreed completely with the relations demanded by these formulæ. Of course, the decomposition is never so complete as the above equation demands.

In carrying out the process it is necessary in the first place that the mixture of oxides obtained by igniting the oxalates should be heated as strongly as possible in a covered crucible, at least to bright redness for some time, so that it may lose all its carbonic acid, and it should be used before it can absorb fresh carbonic acid from the atmosphere. If this precaution is disregarded, it is sometimes quite incapable of acting on the solution of nitrate, even if all other precautions are duly observed. As regards the precipitation of the oxalate it is necessary to proceed exactly as was previously laid down for the precipitation of cerriferous solutions.

The solution to be treated with the oxide must be perfectly free from ammonium nitrate (the above-mentioned washing-waters can therefore serve only for precipitation with oxalic acid, whilst the first filtrates, free from cerium, may be used at once if sufficiently pure), and must of course contain no free nitric acid. Their concentration is preferably such that 1 grm. of oxides is dissolved in 8 c.c. of the liquid.

For instance, 100 grms. of oxide are first ground up dry in a mortar and then worked up to a quite uniform paste with the gradual addition of 100 c.c. of water; 800 c.c. of the solution of the nature above indicated are then added, and the whole is ground up most carefully. The reaction then generally sets in after a short time with a rise of temperature and a considerable thickening of the mass. Whether this takes place or not, the whole is transferred to a deep porcelain capsule, the mortar is rinsed out with 100 c.c. of water, and to complete the reaction the capsule is heated upon the water-bath for 30 to 60 minutes, stirring diligently and crushing any small lumps. The mixture is then allowed to cool a little, the pale, rose-coloured, paste-like mass is then transferred to a tall glass, the capsule is rinsed out with a minimum of tepid water, and the glass is then allowed to stand for 12 hours carefully covered. For extraction the mass is then made up to about 1400 c.c. by the addition of cold water, rendered uniform by means of prolonged and vigorous stirring, and allowed to stand for several days until perfectly clear.

As the basic nitrates eagerly attract carbonic acid, and thus didymium is re-dissolved—

$$3Di_2O_3.2Di(NO_3)_3+9CO_2=3Di_2(CO_3)_3+2Di(NO_3)_3,$$

the access of air should be excluded as far as possible. The solution is then decanted away from the precipitate as clear as possible; the precipitate is again stirred up with about 800 c.c. of water, allowed to settle, and the clear decanted liquid added to the former. It is not advisable to continue washing the precipitate, as in that case it no longer subsides. It is therefore poured upon a filter, the filtrate is returned to the funnel until it runs through clear, and is then permitted to drain, for which 24 hours are often scarcely sufficient.

Solution and precipitate are then further fractionated in a similar manner, the latter being first dissolved in nitric acid to a perfectly neutral solution, applying heat and adding the acid very slowly towards the last. In further fractionation it is advisable not each time to precipitate half the solution with oxalic acid, but in the lanthanum fractions to precipitate a smaller and smaller part in proportion as it becomes poorer in didymium; but in the didymium fractions, on the contrary, to throw down each time a larger and larger portion the more the didymium accumulates.

If, generally speaking, we wish to fractionate a fraction further, so that the proportion of the mixed oxides contained in the precipitate of basic nitrate to that found in the solution to be obtained = n, a portion of the fraction must be precipitated, which is calculated from the formula for the basic nitrate as—

$$\frac{3n}{4(n+1)}.$$

If this fraction reaches the value $\frac{3}{4}$, all the earths are separated out as basic nitrates.

As regards the concentration of the nitrate solution, which must be maintained in the subsequent fractionations, it may be remarked that in the lanthanum fractions we must not fall below a strength of 1 grm. oxide in 8·4 c.c. solution; whilst in the didymium fractions we must not exceed a strength of 1 grm. oxide in 7·5 c.c. of solution, without including the quantities of water above mentioned as required for grinding up the oxide and rinsing out the mortar.

(To be continued.)

* *Berichte der Deutsch. Chem. Gesel*

DETERMINATION OF FERRIC OXIDE AND ALUMINA IN PHOSPHATES.

By R. JONES.

Ten grms. of the sample are dissolved in nitric acid and made up to 500 c.c., 50 c.c. of this solution (=1 grm. of the original substance) are evaporated down to one-half in a beaker, mixed whilst still hot with 10 c.c. dilute sulphuric acid (1 : 5), stirred up, 150 c.c. of alcohol are added, and after again stirring allowed to stand for at least three hours. The calcium sulphate is collected upon a filter and washed with alcohol, filtering into an Erlenmeyer flask holding from 400 to 500 c.c. The washing is complete when the last ten drops, after dilution with an equal volume of water, are no longer reddened by a drop of methyl orange. A small Sprengel pump is very serviceable in washing.

If it is intended to weigh the calcium sulphate, it is laid whilst still moist in a platinum capsule, the filter is laid upon it, the alcohol is burnt away, and the mass ignited with a moderate flame until its weight is constant. The ignited calcium sulphate is not so hygroscopic as to interfere with working in an open capsule.

The alcohol is distilled off from the contents of the flask. It is contaminated with hydrochloric acid or nitric acid and their products of decomposition, and cannot be used again until it has been once more distilled over soda.

The residue from the distillation is washed into a beaker, slightly supersaturated with ammonia, and heated until all the ammonia has been expelled. This precaution is very necessary, as otherwise the precipitate of iron phosphate will be mixed with magnesia.

The residue is collected on a filter; the residues adhering to the glass are swept upon the filter by means of a glass rod tipped with caoutchouc and a jet of cold water. It is washed four times with boiling water poured out from the reversed washing-bottle in order not to stir up the precipitate. In this manner we always obtain clear filtrates. For still greater security a little ammonium nitrate may be added to the washing-water, which of course must not be acid. The precipitate is ignited and weighed.

The precipitate is assumed to consist of ferric and aluminium phosphate, exactly one-half of which is the joint weight of ferric oxide and alumina.

If the operator prefers to determine the ferric oxide and alumina as such, the mixed precipitate when ready for weighing may be dissolved in nitric acid, the phosphoric acid precipitated with the molybdic solution, filtered, and washed; the ferric hydroxide and alumina may be precipitated in the liquid by ammonia and weighed.—*Zeitsch. Anal. Chemie*, xxx., p. 742.

PHOTO-CHEMICAL NOTICES.

By P. ASKENASY and VICTOR MEYER.

In a memoir on the slow combustion of gaseous mixtures, the authors mentioned that V. Meyer and Krause had exposed detonating gas for some months to the light of the sun in closed vessels without any formation of water being observed. No decisive value was ascribed to these experiments, as they were performed during the winter months. We have latterly repeated them, exposing bulbs of detonating gas to solar radiation uninterruptedly from May to October. But here also no change of volume was perceptible on opening the bulbs. It must be added that these results were obtained with the *dry* gaseous mixture. It remained therefore to be examined whether the behaviour of moist detonating gas would be similar.

If therefore a formation of water could not be effected by irradiation alone, it might possibly be produced if detonating gas was exposed to the sun's rays at atmospheric pressure and at a temperature immediately below its point of ignition. For this purpose the intense light of a July sun was concentrated by a large concave mirror, and thrown downwards by means of a metallic plane mirror upon *moist* detonating gas kept at 606° in boiling stannous chloride. Ignition, however, was not observed.

The authors further communicate some experiments undertaken to submit to a renewed test the accuracy of Draper's statements on the photo-chemical induction of chlorine. Draper maintained that a chlorine-detonating gas composed of chlorine and hydrogen previously irradiated possesses the property of combining to form hydrochloric acid even in the dark. Bunsen and Roscoe have rejected this observation as incorrect, showing that chlorine which had been passed outside the laboratory through a glass worm exposed to the rays of the sun, and was then mixed with hydrogen which had been similarly insolated, remained inactive on mixture with the latter in darkness. Against this method of experimentation the objection might be made that the chlorine had been exposed to the chemically active rays for too short a time; possibly a prolonged stage of induction might be required. The authors therefore repeated the experiments in a modified form, exposing chlorine in a long vessel containing 100·5 c.c., and capable of being closed at each end by means of glass cocks for three to four hours to the light of a July sun, the intensity of which was increased by a concave mirror. It was then shaded, the apparatus was placed in a vertical position, and 50 c.c. of hydrogen which had been similarly illuminated were introduced from above from a gas burette, whilst the displaced chlorine could escape at the lower aperture of the apparatus. The analysis of the gaseous mixture which was expelled after some time from the darkened space by means of pure carbonic acid and collected over soda-lye, showed that no hydrochloric acid had been formed, and the exact quantity of hydrogen taken had been recovered. Hence it is demonstrated that chlorine, even if irradiated intensely and for a long time, and hydrogen, similarly treated, do not combine with each other if at once introduced into darkness.—*Justus Liebig's Annalen der Chemie*, cclxix., p. 72.

VOLUMETRIC DETERMINATION OF TELLURIUM.*

By BOHUSLAV BRAUNER.

First Method.

A hydrochloric solution of tellurium dioxide is reduced by stannous chloride, with separation of free tellurium and formation of stannic chloride. The transformation ensues according to the following equations:—

$$TeCl_4 + 2SnCl_2 = Te + 2SnCl_4 . TeO_2 + 2SnCl_2 + 4HCl = Te + 2SnCl_4 + 2H_2O.$$

Brauner prepares the solution of stannous chloride by boiling about 80 grms. granulated tin with about 200 c.c. hydrochloric acid as long as hydrogen is evolved, decants off the liquid, adds to the 150 c.c. thus obtained 450 c.c. hydrochloric acid, and dilutes with water to 1 litre. The solution, which may be further diluted with water, according as larger or smaller quantities of tellurium have to be determined, is preserved in an atmosphere of carbon dioxide. Besides the solution of stannous chloride, there is required a solution of iodine containing per litre 7 grms. iodine and 10 grms. potassium iodide.

For determining tellurium he introduces the hydrochloric solution of tellurium into a measuring flask holding 100 c.c., and adds the solution of stannous chloride whilst applying heat. As long as the latter is not in excess, the liquid is turbid on account of finely pulverulent tellurium, but it clears at once, especially after ebullition,

* *Zeitschrift Anal. Chemie.*

as soon as stannous chloride is present in excess. After the experimentalist has convinced himself by adding a small quantity of stannous chloride that no further precipitation takes place, the flask is filled up to the mark with water which should preferably be free from air, and the air is expelled from the neck of the flask by the addition of a little sodium bicarbonate. The flask is then cooled down to the ordinary temperature, and whilst it is cooling the proportion between the iodine and the stannous chloride solutions is ascertained. When cold the flask is filled up to the mark, and in an aliquot portion of the clear supernatant liquid the excess of stannous chloride is determined by titration with iodine. If particles of tellurium still float in suspension in the liquid, it is first filtered through a dry folded filter, since in presence of hydrochloric acid finely divided tellurium slowly decolourises solution of iodine. The quantity of solution of iodine consumed is re-calculated for the entire volume (100 c.c.), and the corresponding quantity of stannous chloride is deducted from that used for precipitation.

In order to determine the effective value of the solution of stannous chloride, we may, on the one hand, ascertain the proportion of the iodine solution to a known quantity of arsenious acid, and, on the other hand, to the solution of stannous chloride. The following proportion shows the relation of the substances concerned:—

$$As_2O_3 : 4I : 2S_4Cl_2 : TeO_2,$$

i.e., the same quantity of iodine which converts 198 parts (1 mol.) of arsenious acid into arsenic acid, shows the quantity of stannous chloride which reduces 159·6 parts (1 mol.) of tellurium dioxide.

The solution of stannous chloride may also be standardised for a weighed quantity of pure iodine or of pure tellurium dioxide.

The method is said by the author to give useful and approximately accurate results. The solution of stannous chloride is readily oxidised by the action of the air, and its strength decreases during the course of the experiment.

(To be continued).

THE CHEMICAL ANALYSIS OF ALUMINUM.*

By ALFRED E. HUNT, G. H. CLAPP, and J. O. HANDY.

(Concluded from p. 225).

Determination of Chromium in Chromium-Aluminum Alloy.

2 grms. of chromium-aluminum alloy are treated in a 5-inch porcelain dish, with about 50 c.c. of 10 per cent KOH solution. When action has slackened, the solution is boiled up, and finally filtered. The washed residue contains the chromium, together with some silicon, silica, iron, aluminum hydrate, and titanium, if present.

Burn off the filter paper in a porcelain crucible; transfer the residue to a large platinum crucible, and treat with 1 c.c. concentrated H_2SO_4+5 c.c. HF. Evaporate to SO_3 fumes; add 4 grms. bisulphate of potassium; cover the crucible and fuse for about 20 minutes at a low temperature. Finally heat to a high temperature over the blast-lamp to expel nearly all the free acid. Cool a little and add sufficient Na_2CO_3 to make alkaline; also a little KNO_3, and fuse.

Dissolve in hot water and filter. Filtrate contains all the chromium as chromate, together with some alkali aluminate and silicate.

Decompose the latter by warming the solution with NH_4Cl, and filter.

Reduce the chromium in the filtrate, by sodium sulphite or sulphurous acid, and precipitate the chromium as hydroxide by means of ammonia, as usual.

Re-dissolve the $Cr_2H_6O_6$ in HCl; dilute and re-precipitate with ammonia, to free from alkali, taking the usual precautions as to washing free from chlorides in each case.

Weigh as Cr_2O_3.

If the intermediate fusion with bisulphate is omitted, some chromium will not be oxidised.

Method of Analyses of Titanium-Aluminum.

2 grms. of the alloy in a porcelain evaporating dish (5 inches in diameter and covered by a watch-glass) are dissolved by gradual addition of 50 c.c. of "potash solution" (100 grms. KOH in one litre distilled water). Boil for 10 minutes to insure complete solution. Dilute with distilled water to about 125 c.c. Boil up and filter as quickly as possible, washing ten times with boiling water. This filtration separates the iron and titanium quite completely from aluminum. Burn off the residue in a porcelain crucible. Crush it in an agate mortar, and mix with about 8 grms. (6 grms. first, then 2 grms. later) of pure bisulphate of potassium. Fuse in a thin-walled platinum crucible of about 40 c.c. capacity. The cover of the crucible should fit well.

During the first 15 minutes, the crucible should be on a platinum wire triangle over a small flame of a Bunsen burner. The burner flame should be protected from draughts by a sheet-iron chimney, and the flame at first should just touch the crucible bottom. At intervals of 5 minutes remove the cover, carefully invert it (without losing the drop of $KHSO_4$), and place it on a clean stone surface. Then give the contents a rotating motion, holding the crucible firmly in the tongs. At the end of 15 minutes, turn up the light till the lower one-fourth of the crucible is red hot; agitate frequently as before. In ten minutes more, turn on flame full and heat for five minutes, with shaking. Cool, add 2 grms. more $KHSO_4$, and gradually bring to a homogeneous fusion, but do not heat long enough to drive off much free SO_3.

Pour out the liquid fusion into a warmed and dry platinum dish; after the cake cools it will not adhere to the dish. Place it together with the crucible and cover in a 200 c.c. beaker. Add 150 c.c. of water; heat to and keep at 40° C., *with frequent stirring*, until all soluble matter is dissolved. Filter, rejecting the residue, if ignition and treatment with HF show it to be only SiO_2. If it contains anything more, fuse with $KHSO_4$ again.

Estimation of Titanium.

The filtrate contains all the TiO_2 and Fe_2O_3. Add dilute NH_4OH to slight precipitation not re-dissolved by stirring. Add dilute (1 to 3) H_2SO_4 until this precipitate just re-dissolves. Add 4 drops of concentrated H_2SO_4 to the solution, dilute to 250 c.c., and saturate with sulphurous acid gas. Heat slowly to boiling, and boil gently for three-quarters of an hour. Add a little strong SO_2 water occasionally to keep the iron in the ferrous state. Filter through double-washed filters, and wash with hot water. Ignite in porcelain crucible over the blast-lamp.

Weight of $TiO_2 \times 0{\cdot}60 = Ti$.

Estimation of Iron.

In the filtrate from the TiO_2, the Fe is oxidised, precipitated by NH_4OH, filtered and washed, re-dissolved in HCl, and titrated with bichromate. Do not weigh the Fe_2O_3 and Al_2O_3 as precipitated. Attempts to titrate the iron in the sulphate solution occasionally give results which are not accurate.

Estimation of Silicon in Titanium-Aluminum Alloy.

Silicon is estimated just as usual, except that we use a little more HCl (20 c.c.) in re-dissolving after evaporation with H_2SO_4. Under these conditions, no TiO_2 remains with the silica, although it is best to test it, always, with HF and H_2SO_4.

* *Journal of Analytica and Applied Chemistry.*

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.†

CONTENTS :— Introduction. — Balance and Weights.— I. Analysis of Cupric Sulphate; Materials; Description, Three Series; Cause of the Deficiency; Atomic Weight of Sulphur; Atomic Weight of Copper.—II. Synthesis of Cupric Sulphate.—III. Analysis of Cupric Oxide; Tests for Impurities; Determination of Occluded Gases.— IV. Upon Typical Copper.—V. Summary of Results.

INTRODUCTION.

It will be remembered that recent investigation upon the atomic weight of copper has pointed toward the existence of a value for that constant very different from the one indicated by earlier determinations. During the winter of 1886—87 a number of experiments (*Proc. Amer. Acad. Arts Sci.*, xxii., 342) were made in this laboratory upon the replacement of silver from solutions of argentic nitrate by means of metallic copper; and during the following winter these were supported by similar series (*Ibid.*, xxiii., 177; *Fres. Zeitschr.*, xxviii., 392) involving material from different sources. The consistent verdict of all these experiments indicated a considerably higher atomic weight than that which had previously been accepted; but although the new method seemed to be in every way satisfactory, the presumption must nevertheless remain in favour of the older value until the presentation of more evidence against it. Accordingly, another method of determination was devised, and the two distinct but concordant series of results obtained by this method fully confirmed the higher value. The aspect of the case was now wholly changed,— it presented two series of coincidences, of which one must necessarily be due to chance alone; and in such a case certainty can be reached only through a complete and intelligent reconciliation of the conflicting evidence. A careful examination of the possible sources of inaccuracy involved in all recent analyses failed to reveal the probability of a constant error greater than two or three units in the second decimal place. Therefore a complete examination of the older work seemed imperative, and the object of the present paper is to describe such a revision.

A brief review of earlier determinations is given in the first paper of the present series, but for the sake of convenient reference a complete summary is repeated below. On account of the present uncertainty with regard to the ratio of oxygen to hydrogen, the standard to which the figures in the following table are referred is the arbitrary one, O = 16; and this standard has been adopted throughout the present paper.

Atomic Weight of Copper.

O = 16·000.

Berzelius, 1828 (*Pogg. Ann.*, viii., 182), from CuO	Cu = 63·29
Erdmann and Marchand, 1844 (*J. Pr. Chem.*, xxxi., 391), from CuO	63·47
Dumas, 1859 (*Ann. Chim. Phys.*, [3], lv., 129, 198), from CuO and Cu_2S (?)	63·50
Millon and Comaille, 1863 (*Compt. Rend.*, lvii., 147; *Fres. Zeitschr.*, ii., 474), from CuO	63·12
Hampe, 1874, from CuO	63·34
" " $CuSO_4$, (*Fres. Zeitschr.*, xiii., 352; xvi., 458)	63·32
Baubigny, 1883 (*Compt. Rend.*, xcvii., 854, 906), from $CuSO_4$	63·47
Shaw, 1886, through electrolytic equivalent	63·48
" " " corrected (*Phil. Mag.*, [5], xxiii., 138)	63·51
Richards, 1887, 1888 (*Proc. Amer. Acad. Arts Sci.*, xxii., 342; xxiii., 177), by relation to silver	63·60
Richards, 1890 (*Ibid.*, xxv., 195), from cupric bromide (two series)	63·61

The low value obtained by Hampe has been until recently universally accepted, because of the care employed in his analytical work, and the agreement between his results. Hence the present discussion will be confined almost entirely to the two substances which formed the bases of his operations.

The following values for the atomic weights of various elements entering into the present investigation will be assumed throughout the paper.

Oxygen	=	16·000	Hydrogen	=	1·008
Barium	=	137·10	Silver	=	107·930
Bromine	=	79·955	Sodium	=	23·053
Carbon	=	12·002	Sulphur	=	32·060

BALANCE AND WEIGHTS.

The balance used in the work to be described was made with especial care by Henry Troemner, of Philadelphia, and was procured particularly for the present research. The beam and pans are composed of aluminium, and all the remaining metal work is plated with gold. By raising the centre of gravity, the pointer may be made to swing with great constancy as much as eight divisions of the scale for one-tenth of a milligrm.; but since this degree of sensibility is far beyond the range of accuracy obtainable even in atomic weight investigation, the balance was usually adjusted so that the pointer moved ten divisions for a milligrm. A reasonable increase in load altered this relation but slightly. The balance was kept in a small closet lined with curtains, and was protected as much as possible from changes in temperature. The air of the case was dried by means of potassic hydroxide and sulphuric acid, and large dishes of the former substance were kept in the closet outside.

The standard weights have already been described (*Proc. Amer. Acad. Arts Sci.*, xxv., 196). They were carefully rubbed with chamois skin and again compared before the present work. The slight corrections, which scarcely differed at all from those previously found, were applied to each weighing.

A double rider attachment upon the balance made the method of weighing by substitution accurate and easy; and accordingly this method was invariably adopted, except in the first series of experiments upon cupric sulphate. In general, the vessel to be weighed was carefully tared with an adjusted set of common gilded weights, and the vibrations of the pointer were noted. After the removal of the vessel, standard weights were added to the left-hand pan until the same condition of equilibrium was reached. The vessel was then once more substituted for these weights, and any slight change of centre point was of course manifest at once. In the rare cases when such slight change appeared, the weights and vessel were alternately substituted for each other until constancy was reached. In the case of hygroscopic substances, the already ascertained weights were first placed upon each scale pan, then the vessel was quickly removed from the desiccator and substituted for the standard weights, and, finally, the latter were again put in place.

All desiccators were allowed to remain in the closet with the balance three or four hours before the weighing, and objects were often weighed on successive days, to furnish assurance of constancy. In every case the barometer and thermometer were read, and any correction due to change of relative buoyancy amounting to more than the fiftieth of a milligrm. was applied to the result. With large vessels an invariable slight loss of weight, amounting

* Contributions from the Chemical Laboratory of Harvard College From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† For a previous paper on this subject, by the same author, see CHEM. NEWS, vol. lxiii., p 20.

sometimes to as much as one-twentieth of a milligrm., was noticed after the object had remained for some time upon the balance pan. The loss may have been due to the replacement of the perfectly dry air from the desiccator by the less completely dried air of the balance case. Possible error from this source was avoided by the employment of uniform conditions suited to the particular substance in hand.

All weighings were of course reduced to the vacuum standard by calculation from the specific gravities of the substances and weights involved (*Proc. Amer. Acad. Arts Sci.*, XXV., 196. Specific gravity of brass =8·3). Through the great kindness of Professor Mendenhall, of Washington, two of the laboratory's ten-grm. weights (one of brass and one of platinum) have been compared as carefully as possible with the standards of the Washington Bureau of Weights and Measures. Five comparisons of the Sartorius ten-grm. weight with these gave the following results for its value in vacuum :—

1891.		Grms.
Feb. 4.	By comparison with the brass weight	10·00025
Mar. 4.	„ „ platinum „	10·00025
Mar. 14.	„ „ „ „	10·00026
June 12.	„ „ „ „	10·00026
June 12.	„ „ „ „	10·00024
	Average	10·00025

The third and fifth of these comparisons were made with the balance in the condition of greatest sensibility, while the others were made exactly in the usual manner. It is not pretended, however, that all the weighings which follow have probable errors so small as these. The results are nevertheless an excellent gauge of efficiency of the balance, especially since the observations were made at widely varying temperatures and pressures. The correction involved, applying in the same proportion to all weighings, has been omitted from the following figures; but any weight given below may of course readily be reduced to the Washington standard by multiplication with the factor 1·000025.

(To be continued).

OBITUARY.

THE LATE PROFESSOR A. W. von HOFMANN.

The scientific world has received a painful shock by the death of August Wilhelm von Hofmann, which took place the 5th inst. The deceased was beyond question one of the foremost chemists of the time; widely and honourably known, both for his brilliant researches in some of the most interesting departments of organic chemistry, and for his successful career as a teacher of his science both in Germany and England.

Like so many other young chemists of the second quarter of the century, Hofmann received his training at the University of Giessen, under Liebig, and then took up the study of the coal-tar bases and their metamorphoses. In 1848, at Liebig's recommendation, he was appointed Professor at the Royal College of Chemistry in London, then just called into being. His career here was eminently successful. He was found to have imbibed the spirit of his master Liebig, and the laboratory of the Royal College became, under his guidance, a school of chemistry similar in its efficiency to that of Giessen. Not a few of the most eminent English chemists were trained under his directions, and we are justified in saying that they one and all retain a grateful recollection of his patience, his perseverance, and his kindly interest in their progress. We had previously had in Britain chemists of the highest merit, but in the Royal College of Chemistry we had for the first time a school of chemistry on a level with the requirements of the day. Hofmann remained in London till 1864, having been in the meantime appointed (1855) to the Wardenship of the Royal Mint. In 1864 he was called to the chemical professorship at the University of Bonn, and in 1865 he was appointed to the chemical chair at the University of Berlin. Here he renewed his activity. Besides continuing his researches on the coal-tar bases, especially rosaniline, he distinguished himself by his success as a teacher and by his efficiency as one of the foremost scientific advisers of the German Government whenever chemical questions were concerned. He took an active part in the organisation of the German Chemical Society, and was its President at the time of his death.

Recognition of his merits was not wanting. In 1851 he was elected a Fellow of the Royal Society, and in 1854 he became a recipient of the Royal Medal in especial consideration of his "Researches on the Molecular Constitution of Organic Bases. In 1875 he received from the Royal Society the Copley Medal—the "blue ribbon" of science. He has been President of the Chemical Society of London, and was up to his death one of its vice-presidents.

Although Hofmann felt it a duty to accept the positions offered him in his native country, he always looked back with pleasure to his sojourn in London and to the numerous and attached friends he had gained here. In both countries he will be deeply and widely regretted.

NOTICES OF BOOKS.

Elements of Materia Medica and Therapeutics; Including the whole of the remedies of the British Pharmcopœia of 1885 and its Appendix of 1890. By C. E. Armand Semple, M.B., M.R.C.P. London: Longmans, Green, and Co.

By far the greater portion of this work can be appreciated only by the medical and pharmaceutical world. It is interesting to note that certain vegetable matters which enjoy a high reputation among the general public here figure less prominently. Thus bael fruit is pronounced "probably not superior to some other vegetable astringents." Even the wonder-working chirata or chiretta—as it is represented by certain vendors of proprietary nostrums—is here described as "acting exactly like gentian."

A painful fact is the uncertainty which seems to prevail concerning the properties of many drugs. Again and again we read: "It is said to act"; "it is said to be antidotal, &c."

Many of the illustrations are calculated to be exceedingly useful for the identification of medicinal plants, but we fail to see the reason for figures of a pig, a sheep, or an ox.

As far as chemical compounds are concerned, it is very unsatisfactory that medical writers still employ a distinct nomenclature—distinct from that employed for scientific purposes, and from the industrial terminology.

Blowpipe Analysis. By J. Landauer. Authorised English Edition, by James Taylor, B.Sc. Second Edition, Revised and Enlarged, 1892. London: Macmillan and Co.

The appearance of this book we may regard as a sign that more attention is being turned to the use of the blowpipe in inorganic analysis. On the value of this little instrument, both for preliminary testing and often as the only available guide for the prospector, the mining engineer, &c., when obliged to work in situations where the appliances of a regular laboratory are not available, it is needless to enlarge.

The author treats in succession of apparatus and reagents, and of the operations in blowpipe analysis, with

an appendix on Bunsen's flame reactions. An important improvement here is the use of the spectroscope in the not unfrequent case that several flame colouring elements occur together. Browning's direct-vision pocket spectroscope is recommended as most serviceable for blowpipe work, and it will certainly not form any appreciable addition in bulk or weight to the outfit of a travelling explorer.

Chapter III. gives directions for special examinations for certain elements in combination.

In Chapter IV. we have two systematic courses of examination for compound inorganic substances, Landauer's own and Egleston's.

In conclusion there are a condensed view of blowpipe reactions and a tabular view of the behaviour before the blowpipe of the alkalies, earths, and metallic oxides, whether alone or with reagents.

This little work deserves the highest recommendation for its clearness, comprehensiveness, and portability.

A Summer School of Art and Science. Summer Meeting, Edinburgh. (*Vacation Studies*). Sixth Session, August 1st to 31st. University Hall, Edinburgh, Easter, 1892.

We have not often met with a prospectus which called up in our mind such sympathetic interest as does the present. The idea of utilising a part of the long university vacations for studies of a peripatetic and open-air character is not indeed novel. At some of the German polytechnic schools the curricula include excursions to places of geological or botanical interest, as well as to interesting industrial establishments, mines, smelting and refining furnaces, tinctorial works, &c. And at some of the universities a party of students during vacation will sometimes get up among themselves an exploring expedition, in which they proceed as if investigating an unknown country. These excursions, though sometimes accompanied by a professor, are perfectly unofficial.

"Summer schools" have also been organised in the United States, though one of these gatherings, held at Concord a few years back, rendered itself unpleasantly conspicuous by its anti-evolutionary, or rather anti-scientific, utterances.

But Edinburgh may claim the credit of having taken up these scattered threads and woven them into a complete tissue. The movement seems to have attracted attention abroad since last year. The French Minister of Public Instruction deputed two eminent *savants*, Prof. Espenas, of Bordeaux, and Dr. Henri de Varigny, of Paris, to investigate and report on the scheme. This year it is hoped that lectures will be delivered by Professor Haeckel, of Jena, and Dr. de Varigny, of Paris.

We cannot give a summary of the intended proceedings without reprinting a considerable part of the prospectus. But there are not a few points which we must notice with satisfaction.

Thus political economy will be taught not by men contemptously ignorant of the physical and natural sciences, but by such men as Prof. Geddes. The principle of Evolution will be applied in the courses of literature and anthropology. Thus in the latter department the infant will be considered as parallel to the anthropoid, and the child to the savage. The criminal will be viewed as a case of arrested development or of reversion.

In Art, "the study of landscape and animal life is definitely associated with the school of natural science, and that of (human) figure with anthropology and history, the student thus working for the artist, and the artist for the student."

Another laudable feature is the extent to which mere book-learning or verbalism is to be superseded or at least modified by actual familiarity with the objects or processes to be explained. Many of the lessons will be given in the museums (scientific and industrial), at the Granton marine station, in mines, and in places of geological interest, which are certainly not lacking in the Edinburgh district.

It is impossible to examine this prospectus without sharing in the hopes of the promoters that a step is being taken which will lead to the solution of the pressing educational problems of the present age.

The fee for the entire course is £3 3s. Gentlemen may board in University Hall, Mound Place, at 21s. to 26s. weekly; whilst ladies may be accommodated at the same rates at University Hall, Riddle's Court.

Throughout the entire prospectus there is no reference to any "syllabus" or examination. The student is evidently called upon not to cram his memory, but to cultivate his faculties of observation and to assimilate methods. On the title-page of this pamphlet there is a design of birds flying, but they are evidently not Strassburg geese.

Agricultural Research Association for the North-Eastern Counties of Scotland. New Organisation, 1891.

This report by Mr. Thomas Jamieson contains no little interesting information. We are told in the introduction, and with too much truth, that "the tendency of the age is to regard as an essential feature of success a speedy return for outlay." This feeling, the author justly urges, should be resisted as fatal to success. Sound research, whether its ultimate object be theoretical or practical, cannot be hurried.

It is found that experimental stations should be not merely enclosed, but even covered over with a bird-proof wire netting. Some of the plots had to be twice re-sown, as whole drills had been systematically cleared of their plants. It is a question not taken up by the author, but we might ask whether the purely zöophagous birds, such, *e.g.*, as the wag-tails, could not be encouraged at the expense of the phytophagous species?

As a complete manure Mr. Jamieson recognises one supplying nitrogen, phosphorus, and potash. Hence he does not agree with M. Ville in placing lime in the same rank with the three above-mentioned substances.

He still holds that manures containing sulphuric acid, such as dissolved bones, superphosphate, &c., is the main cause of the "club-root" disease in turnips. As a mixture for turnips he recommends 1 part each of steamed bone-flour, of nitrate of soda, and nitrate of potash, 4 parts ground coprolite, and 6 parts basic slag. We are somewhat sceptical as to the value of undissolved coprolite. Slag, it appears, is now adulterated with the Redonda phosphate, which is of marvellously little—if any—value as plant food.

In an interesting inquiry on the function of the root-hairs of plants, it is suggested that plants take up their solid food in the solid form through the air-root apertures.

A Practical Introduction to Chemistry. Intended to give a Practical Acquaintance with the Elementary Facts and Principles of Chemistry. By W. A. Shenstone, Lecturer on Chemistry in Clifton College, 1887. London: Rivingtons. Small 8vo., pp. 108.

This little work is said to be a "new edition," and to have appeared in 1887, though it is only now sent for notice. The author has previously done such good service by the production of his "Methods of Glass-Blowing" that we cannot do other than regret that he should have spent his time in adding one more to the existing swarm of elementary treatises on chemistry.

We are weary of asking ourselves, that such books are more plentiful in Britain than in other civilised countries, how is it that publishers can always be found for them? and other painful questions. It is certain that the crop can bear no definite proportion to the seed sown, otherwise we should be richer than any of our neighbours in chemical discoverers, inventors, and industrialists. Such, we need scarcely say, is by no means the case. Is it possible that these books are an indirect product of the dominant examinational system? The author's introductory chapter contains much that is decidedly valuable.

Sanders's Question Compends, No. 2. Essentials of Bacteriology; Being a Concise and Systematic Introduction to the Study of Micro-organisms for the Use of Students and Practitioners. By M. V. BALL, M.D. With 77 Illustrations, some in colours. Small 8vo., Pp. 159. Philadelphia: W. B. Saunders. 1891.

THIS work is, as it professes, a concise introduction to the study of micro-organisms,—those at least belonging to the vegetable world. Its appearance is a proof of the increased attention which the physician and the sanitarian are now paying to the study of those ultra-microscopic beings some of which rank among our most formidable enemies. As far as the subject matter is concerned the author has performed his task well, very few statements being found to which exception may be fairly taken. It may, perhaps, be submitted that the dependence of Beggiatoa on sulphur is not brought into sufficient prominence. This unlovely plant is, indeed, sometimes found "where the remains of organic life are decomposing," but only where such remains contain a sufficiency of sulphur.

The author's language offers ample room for improvement. We do not notice the frequent errors, clerical or typographical, in proper names except where they may occasion confusion. Thus we find mention of the "Chamberland" filter and also of that of "Chamberlain." It is possible for a student to suppose that we have here to do with two different filters. It might also be doubted whether Van Tieghaim and Van Tiegham were or were not identical. In reality they are both incorrect versions of one name, Van Tieghem. We must decidedly object to such words as "aerobins" and "anaerobins." The correct English words would, we submit, have been "aerobians" and "anaerobians." The expression "aniline oil" is very needless; aniline when existing in a free and non-modified state is of course a liquid of a somewhat oily appearance, but nothing save needless complication is gained by always keeping this fact before the reader. Certain abbreviations are doubtful, *e.g.*, "*tr. iodine*," also "6 *gtts.* of turpentine" and "5 *gtts.* of safranin (Bismark-brown"). We hope that Bismarck-brown is not here given as a synonym for safranin.

Not a few passages in the work will expose the writer to vituperation from the opponents of physiological experimentation, who will dub him an "artist in filth and torture." However, he will not be the only man who has been maligned for seeking to extend the dominion of Science.

The work before us will, we hope, induce many students to enter upon a deeper investigation of the "infinitely little."

The Pharmaceutical Review, Vol. I., Nos. 1, 2, and 3. THIS new journal, though ably edited and written, contains very little which can legitimately come under our notice. It is a business organ, having for its principal function to maintain the rights of the pharmacist in America as against his foes, the "cutter," the "jobber," the fussy meddler, and, above all, the quack. Whether he has also, like his British colleagues, to make head against the encroachments of the monopolist draper we do not learn. The new review and the body it advocates have our best wishes.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 17, April 25, 1892.

Means of Artificially Occasioning Rain.—M. Faye.—The means proposed are fires or explosions. The author concludes that there is a radical distinction between ascending currents of hot air and tornadoes, and regards the hopes entertained of producing rain at will as illusory.

Analysis of a Chromiferous Clay from Brazil.—A. Terreil.—Chromium sesquioxide is present only to the extent of 1·69 per cent.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. xvii., No. 1.

Densimetric Determination of Phosphorus in Cast Irons.—E. Metz.—A modification of the process published by R. Popper in the *Zeit. fur Anal. Chemie*, vol. xvi., p. 157, and vol. xviii., p. 14. The weight of a precipitate is determined on the densimetric method, according to the following equation—

$$x = \frac{S}{S-s}(G-g).$$

where S is the specific gravity of the precipitate, s the specific gravity of the solution in which the precipitate is present, G the weight of the picnometer containing the solution and the entire precipitate, g the weight of the picnometer containing the solution alone, and x the weight of the precipitate to be determined. The value S is supposed to be known, G and g are found by weighing, and s by calculation. For the specific gravity of four determinations the author gives as a mean 3·252. He objects to the gravimetric method on the grounds that the precipitate of ammonium phospho-molybdate is not absolutely insoluble in the liquids used for washing, and that the drying the precipitate affects its constitution.

Bulletin de la Société Chimique de Paris. Series 3, Vols. vii. and viii., No. 7.

Action of Acetic Anhydride upon Dimethylaniline.—F. Reverdin and Ch. de la Harpe.—Acetic acid reacts upon dimethylaniline at common temperatures and in presence of air, occasioning the formation of tetramethyldiamidodiphenylmethane.

Action of Secondary Capryl Iodide upon Trimethylamine in an Aqueous Solution and in Equimolecular Proportion in the Cold. Formation of Caprylene and Trimethylamine Hydriodate.—H. and A. Malbot.—In the cold there are formed only two products, caprylene and trimethylamine hydriodate, whilst in heat there are formed in addition dimethylcaprylamine and tetramethylammonium iodide.

Nitrised Butyltoluene- and Butylxylene-sulphonic Acids.—E. Noelting.—It is a general fact that the sulphonic acids of strongly odoriferous bodies are absolutely scentless. Of this we have numerous examples in all classes of bodies. Thus benzene, naphthalene, nitrobenzene, aniline, naphthylamine, quinoleine, benzaldehyd, phenol, naphthol, biiodophenol, have all very decided odours. Their sulpho-conjugated acids in a pure state are absolutely inodorous.

Assay of Ores of Antimony.—Ad. Carnot.—Already inserted.

Reduction of the Nitrates of the Aromatic Amines and their Transformation into Chlorinated Hydrocarbons.—M. Prudhomme and C. Rabaul.—This paper does not admit of useful abstraction.

Novel Synthesis of Tartaric Acid.—P. Genviesse.—The author treats glyoxylic acid with zinc-powder in presence of acetic acid diluted with its own weight of water, firstly at common temperatures and then in the water-bath. The filtered liquid is treated with potassium carbonate, and after the precipitate has been filtered off, with calcium chloride. The white precipitate formed has all the characters of calcium racemate.

Determination of Potassa.—F. Jean and M. Trillot.—Instead of sodium formiate the authors propose to use a solution of formic aldehyd.

MISCELLANEOUS.

Institute of Chemistry.—A Conference of the Members of the Institute will be held at the Rooms of the Chemical Society, Burlington House, at 3 p.m., on Monday, May 16. The subject for discussion will be: "The Present Regulations with Respect to the Admission of Fellows and Associates to the Institute."

Congress of German Naturalists and Physicians.—This body, the oldest of the itinerating associations for the advancement of science, will hold its 65th meeting at Nuernberg, from September 12th to 16th. Memoirs, &c., to be produced should be announced before the end of May, as the general invitations will be sent out in the beginning of July.—*Chemiker Zeitung.*

Researches on the Adherence of the Various Cupriferous Dressings used to Combat Fungoid Diseases in Plants.—Aimé Girard.—In heavy rains certain of the preparations used to combat the potato-disease and the mildew of the vines have been washed away and have in consequence proved ineffectual. The most easily displaced among these preparations was the well-known "Bordeaux broth" (copper sulphate 2 kilos., slacked lime, weighed as quicklime, 2 kilos., water 100 litres). The most resistant are the "Burgundian broth" (copper sulphate 2 kilos., soda-crystals 3 kilos., water 100 litres), the formula of Michael Perret (copper sulphate 2 kilos., lime 2 kilos., treacle 2 kilos., water 100 litres), and a mixture which has been successfully employed at Montpellier, consisting of bibasic copper acetate stirred up in water (verdigris 1 kilo. 600 grms., water 100 litres).—*Bull. Soc. d'Encouragement pour l'Industrie Nationale*, viii., No. 75.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Spontaneous Breaking of Glass.—On the night of Friday, the 29th of April, about 10 o'clock, a remarkable thing happened here. An ordinary cut crystal tumbler containing a little drinking water, standing on the sideboard, cracked with a very loud report. The conditions in the room were nominal, but the tumbler was near a window looking to the north, and at the time there was a brilliant display of aurora borealis. It would be very interesting to know the cause of this accident, and I shall be pleased to give any of your curious readers any other information.—B. S.

Respiration of Plants and Animals—(Reply to I. L.).—The apparent contradiction pointed out by your correspondent "I. L." is very clearly explained in Bennett's Edition of Thomé's "Botany." The misunderstanding arises from a loose application of terms. In the process of assimilation plants absorb carbon dioxide and decompose it with the elimination of oxygen, the carbon being retained and built up into the plant tissues. In the process of respiration plants absorb oxygen from the atmosphere, not, however, in order to assimilate it, but, on the contrary, in order to decompose the substances contained in the plant, to deprive them of at least a part of their carbon, the products of this action being then exhaled as carbon dioxide. Respiration is therefore a process diametrically opposed to the process of assimilation. To describe them under the same name is as incorrect as if we were to speak of an animal inhaling its food.—Henry B. Woodall.

Respiration in Plants and Animals—(Reply to I. L.).—I am unable at the moment to give the name of any book which accounts for the apparent contradiction mentioned in last week's issue of the Chemical News by your querist "I. L.," but the following is the received explanation. All living organisms, whether animal or vegetable, as a necessary result of those processes of oxidation without which life is impossible must exhale carbonic anhydride as a final product. This is a respiratory action, and in the case of animals and of plants containing no chlorophyll (*e.g.*, most fungi) this elimination of carbonic anhydride is easily demonstrated. When, however, we turn to the chlorophyll-bearing plants, we find this action masked by another, not respiratory, but assimilative. These plants have, by means of their chlorophyll, the power in the light of absorbing carbonic anhydride, and with the aid of the elements of water-producing carbohydrates such as cellulose, starch, and sugar, with the elimination of oxygen. Disregarding intermediate reactions, this equation is typical, $6CO_2+10H_2O=C_6H_{10}O_4+6O_2$. In the light this assimilative action so preponderates over the other, the respiratory, as to mask it completely, but, in the absence of light, the chlorophyll becomes inactive, and then in chlorophyll-bearing plants, as the assimilative process has ceased, the exhalation of carbonic anhydride may be demonstrated as in the case of animals and fungi.—A. Percy Hoskins, F.I.C.

MEETINGS FOR THE WEEK.

Monday, 16th.—Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Industries," by Percy F. Frankland, F.R.S. (Cantor Lectures).
Tuesday, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30. (Anniversary).
—— Society of Arts, 8. "Mud, a Material for Architecture in Persia and the East," by William Simpson, R.I.
—— Royal Institution, 3. "Photography in the Colours of Nature," by Frederick E. Ives.
Wednesday, 18th.—Society of Arts, 8. "Colour Blindness," by Capt. W. de W. Abney, F.R.S.
—— Microscopical, 8.
—— Meteorological, 7.
—— Pharmaceutical, 11 a.m. (Anniversary).
Thursday, 19th.—Royal, 4.30.
—— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.
—— Institute of Electrical Engineers, 8.
—— Society of Arts, 4.30. "The Administration of the Imperial Census of 1891 in India," by Jervoise A. Baines, I.C.S.
—— Chemical, 8. "Magnetic Rotation of some Acetyl Derivatives," by W. H. Perkin, F.R.S. "Studies in Isomeric Change. No. IV.—Halogen Derivatives of Quinone, Part I.," by A. R. Ling. "Note on Diastatic Action," by E. R. Moritz T. A. Glendinning. "Formation of the Hydrocarbon $C_{18}H_{12}$ from Phenylpropiolic Acid," by Dr. Kipping.
Friday, 20th.—Royal Institution, 9. "Electro-Metallurgy," by J. Wilson Swan, M.A., F.C.S.
—— Quekett Club, 8.
Saturday, 21st.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

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Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents, issued on the 4th May, 1892.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment, within one calendar month from the date of the said Journal.

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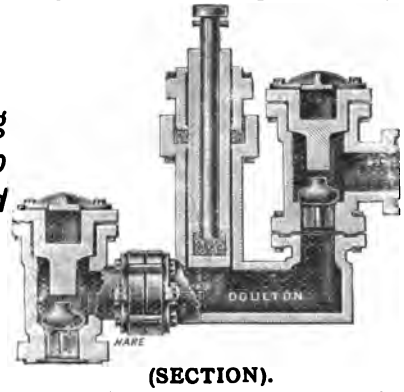

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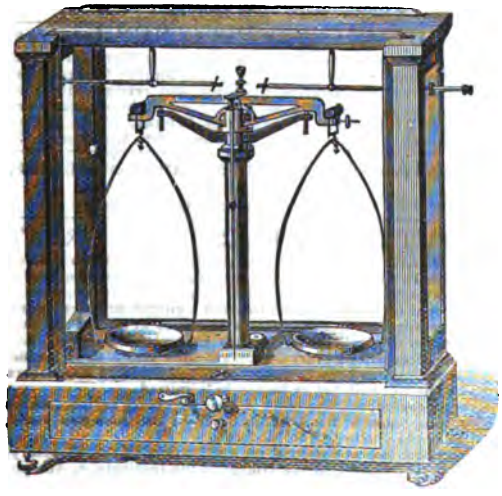

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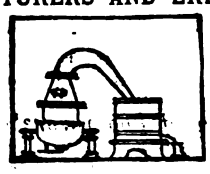

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Having to constantly use Kjeldahl's process for the estimation of nitrogen in manures and numerous substances, I have attempted by various modifications to render the method more accurate and rapid, and as the following notes may be of interest I venture to publish them.

It is well known that many substances used as artificial fertilisers contain nitrogen in three distinct forms, viz., organic, ammoniacal, and oxides of nitrogen; and for the estimation of the first two the ordinary process answers very well, but when the substance contains nitro-oxides the results are unsatisfactory.

It occurred to me that it might be possible to combine the ordinary Kjeldahl process with a method by which nitrates are analysed. The principle of the method to which I refer is the reducing action of nascent hydrogen on a nitrate in solution. Though to all appearance this method is easily carried out, the practical difficulties are great; it is a somewhat delicate operation to heat for a considerable time a glass flask containing a quantity of zinc and iron filings without risk of fracture; I therefore thought that by using a flask of iron containing granulated zinc, or rather zinc grains, the process might be rendered much safer, and at one and the same operation all nitrogen in whatever form might be estimated.

To begin with I made experiments carrying out the ordinary Kjeldahl process in a flask of thin iron with a coating of tin such as are used for oil, &c. Having procured some substances the nitrogen in which was known,—to give an example, in a manure which contained 11·00 per cent of ammonia,—I found 11·37 per cent, a result which is excessive; but on making three estimations in blank, I found that on an average a deduction of 0·00176 grm. of ammonia might be made from the result; this being done the final result is 11·08 per cent of ammonia, which is within the limit of error.

The small quantity of ammonia is not contained in the reagents, but is formed by the action of the moist oxide of iron in the flask on the air, the flask being always moist after an experiment.

Among advantages of iron flasks are that heat can be applied strongly at once, and the analysis is finished sooner; also, that after starting the operation requires little or no looking after till the conclusion. To be sure the distillate is not always quite clear, but a plug of cotton-wool in the bulb tube which joins the flask as usual to the condenser in a measure averts this; nor are the iron flasks permanent, but for that matter few things are in a laboratory or elsewhere, and the cost is a trifle.

For substances which contain small quantities of nitrates this method is very successful, and a minute though important amount of nitrogen is thus rescued from being passed over. In the analysis of soils, for instance, comparatively large quantities can be treated this way, and greater accuracy obtained. I may state that there is no novelty here except in the application, as Arabian chemists many centuries ago used flasks of metal, copper for instance.

It is well to use the same quantity of sulphuric acid in each preliminary digestion, say 20 c.c., also a known sufficiency of strong soda solution, making the acid liquid dilute before adding to the flask 20 c.c. of a 40 per cent solution of potassium sulphide as usual. If the distillate is not clear it can be filtered through an English paper, but this is hardly ever necessary. Three or four blank distillations, the lapse of one night between each, will give an average quantity of ammonia to deduct in each case, and indeed this peculiarity is rather of service than otherwise, as it makes the titration more certain in cases where the amount of ammonia is very small.

Lawes' Works, Barking, May 13, 1892.

ACTION OF AMMONIC CITRATE ON HIGH GRADE ALUMINIC PHOSPHATE.*

By H. A. HUSTON,

In the latter part of July a sample of high grade aluminic phosphate was submitted to me for analysis. The results desired were the amounts of total and of "available" phosphoric acid present. As the material was quite different from the ordinary fertiliser stock, a series of experiments were made to determine the effects of varying the conditions used in the official method for available. Three methods for determining total phosphoric acid were used, and gave closely agreeing results.

The material was stated to be anhydrous phosphate of aluminum, which had been calcined. It was found to contain 45·46 per cent of phosphoric acid and 7·25 per cent of silica. There was no soluble phosphoric acid present in the sample. The work on available phosphoric acid was made by using in all cases 100 c.c. of the official citrate solution. In the fourth series solid citric acid and ammonic hydrate were added. The results appear in the following tables:—

Series I.—*Effect of Increasing the Time of Digestion.*

(Amount taken, 2 grms.; temperature, 65° C.; 100 c.c. citrate solution).

Time of digestion.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
One-half hour	21·24	46·75
One hour	31·70	67·53
Two hours	36·92	81·10
Four ,, ...	40·80	89·67
Six ,, ...	41·00	90·11
Ten ,, ...	42·70	93·85

Series II.—*Effect of Changing the Temperature at which the Digestion was Conducted.*

(Amount taken, 2 grms.; time, thirty minutes; 100 c.c. citrate solution).

Temperature.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
40° C.	2·18	4·79
50° C.	5·52	12·10
65° C.	21·24	46·75
75° C.	32·90	72·30
85° C.	39·52	87·90

Series III.—*Effect of Changing the Amount of Phosphate Taken.*

(Temperature, 65° C.; time, thirty minutes; 100 c.c. citrate solution).

Amount of phosphate taken.	Per cent dissolved.	Fraction of tota phosphoric acid dissolved.
½ grm.	16·80	36·9
1 ,, ...	18·26	40·1
2 grms.	21·24	46·7
3 ,, ...	23·22	51·0
5 ,, ...	24·66	54·2
10 ,, ...	28·64	62·9

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

SERIES IV.—*Effect of Making the Citrate Solution Acid or Alkaline.*

(Amount taken, 2 grms.; time, thirty minutes; 100 c.c. citrate solution).

Amount of acid or alkali added to the solution.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
2 grms. citric acid	17·21	37·21
1 grm. „ „	18·26	39·49
0·75 grm. citric acid	17 84	38·58
0·50 „ „	19·98	43·20
0·10 „ „	21·08	45·60
0·05 „ „	21·14	45·70
Neutral solution..	21·32	46·10
Ammonia enough to neutralise 0·05 grm. citric acid	23·44	50·70
Ammonia enough to neutralise 0·10 grm. citric acid	24·38	52·70
Ammonia enough to neutralise 0·50 grm. citric acid	26·02	56·30
Ammonia enough to neutralise 1·00 grm. citric acid	30·78	66·60

The only set of the above results that seems to require any special comment is Series III., where the results are rather unexpected. The work in this direction will be continued in order to find out whether the peculiar effect is due to the fact that the digestion is stopped before the solution is complete, or whether a solution of aluminic phosphate in ammonic citrate really has a greater solvent power than the original solution of ammonic citrate.

The commercial importance of this matter will appear from the following:—Suppose the high grade phosphate is used in making up goods to the extent of one-fourth their weight. Then there should be 5·31 per cent of available derived from the aluminic phosphate. But if the results in series are correct there would appear on analysis only 4·20 per cent of available from this source.

The matter is also of considerable interest from a purely scientific standpoint.

VOLUMETRIC DETERMINATION OF TELLURIUM.*

By BOHUSLAV BRAUNER.

(Concluded from p. 235).

Second Method.

THE author attempted to found a further volumetric determination of tellurium upon the oxidation of tellurous acid to telluric acid by means of chromic acid or potassium bichromate. In these experiments a hydrochloric solution of tellurous acid diluted with water was mixed with a solution of potassium bichromate in excess, and after some time the excess of bichromate was titrated back with an acidified solution of ammonium ferrous sulphate.

The oxidation of the tellurous acid is the more complete the greater the volume of the solution of chromate originally added, the larger the quantity of hydrochloric acid present, and the more prolonged the action. The oxidation is effected very slowly, and only approximates on completion after an hour. The main reaction is accompanied by a disturbing secondary reaction, which is recognised by a slight odour of chlorine or of ozone. A decomposition of the solution containing hydrochloric, chromic, and telluric acids takes place at the expense of a small quantity of chromic acid, whereby the results are rendered rather too high. The method possesses, therefore, theoretical possibility, but only a slight practical value.

*Zeitschrift Anal. Chemie.

Third Method.

Attempts to determine tellurium iodometrically by the action of solution of iodine upon alkaline solutions of tellurous acid (alkaline tellurites), proved failures, as the oxidation of tellurous acid by iodine is only gradual. A complete oxidation may certainly be effected by prolonged action with the aid of heat, but the excess of the iodine added cannot be accurately determined.

Fourth Method.

Since the behaviour of tellurous acid with chromic acid in a hydrochloric solution, and with iodine in an alkaline solution, shows that the oxidation to telluric acid proceeds but slowly, the author tried the use of a more energetic oxidising agent, permanganate.

Attempts to determine tellurous acid in a hydrochloric or sulphuric solution by titration with solution of permanganate gave no satisfactory results, since in the reaction along with the formation of manganic chloride or sulphate there always took place a liberation of chlorine or ozoniferous oxygen. The inevitable development of oxygen and the excessive consumption of solution of permanganate thus occasioned led always to false values. Useful results could be obtained by this method only if an especial correction is introduced, or if the solution of permanganate is standardised under the same conditions with a weighed quantity of tellurium dioxide.

Decidedly better results were obtained on titrating tellurous acid with permanganate in an alkaline solution, as here no escape of free oxygen or ozone is to be observed. The oxidation of tellurous acid ensues according to the following equation—

$$2KMnO_4+3TeO_2=K_2O+2MnO_2+3TeO_3.$$

In reality there is formed an alkaline tellurate, and perhaps a compound of telluric acid and manganese.

In the practical execution of this process decinormal potassium permanganate is added to the alkaline solution of tellurium dioxide until the former distinctly predominates. The solution is then mixed with an excess of dilute sulphuric acid, and so much decinormal oxalic acid is added that its volume corresponds to about half that of the permanganate added. On applying heat, the higher oxides of manganese dissolve, whilst the liquid becomes completely colourless, and may be titrated with solution of permanganate at 60° in the known manner.

The titration is effected in an alkaline solution without the escape of oxygen, but on the addition of sulphuric acid a faint but distinct odour of ozone is apparent. The excessive consumption of permanganate thus occasioned does not on an average amount to more than 0·35 per cent. If decinormal oxalic acid is used for standardising the solution of permanganate the factor must be diminished by this small quantity. If the permanganate is standardised with pure tellurous acid this correction is, of course, dispensed with.

If tellurium dioxide has to be determined in a hydrochloric solution either the first method may be used or the following process. The hydrochloric solution is evaporated down on the water-bath with a little sulphuric acid, and the highly concentrated solution is heated for some time on the sand-bath in order to expel the last traces of hydrochloric acid. There is no reason to fear any appreciable loss of tellurium tetrachloride by volatilisation. The dilute solution is then supersaturated with pure sodium hydroxide, and titrated with permanganate as above described.

According to the author, the determination of tellurium with permanganate is both more exact and expeditious than all previous methods.

A Soluble Naphtholic Compound.—M. Stackler.—The compound obtained, for which the name asaprol is proposed, seems to be serviceable for destroying the microbes of cholera, typhoid, and splenic fever.—*Comptes Rendus*, cxiv., No. 18.

RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

(Continued from p. 233).

THE process of fractionation followed with the 808 grms. of earths free from cerium can be seen in the following conspectus. The approximate quantity of oxides is appended in most fractions.

The colour of the highly concentrated solutions of the nitrates prepared from the eight fractions obtained was:—In the fraction Di III. a_1, which must contain all the earths of the feeblest basicity, a rather dark dirty violet-rose; in the intermediate fractions, a rather lighter and purer violet-rose; in fraction La III. b_2, almost colourless by daylight, but by gaslight a very pale rose; finally, in fraction La III. b, a greenish yellow by daylight, but a dirty rose by gaslight. In this fraction, therefore, the oxide process had already effected a perceptible splitting up of didymium into its components.

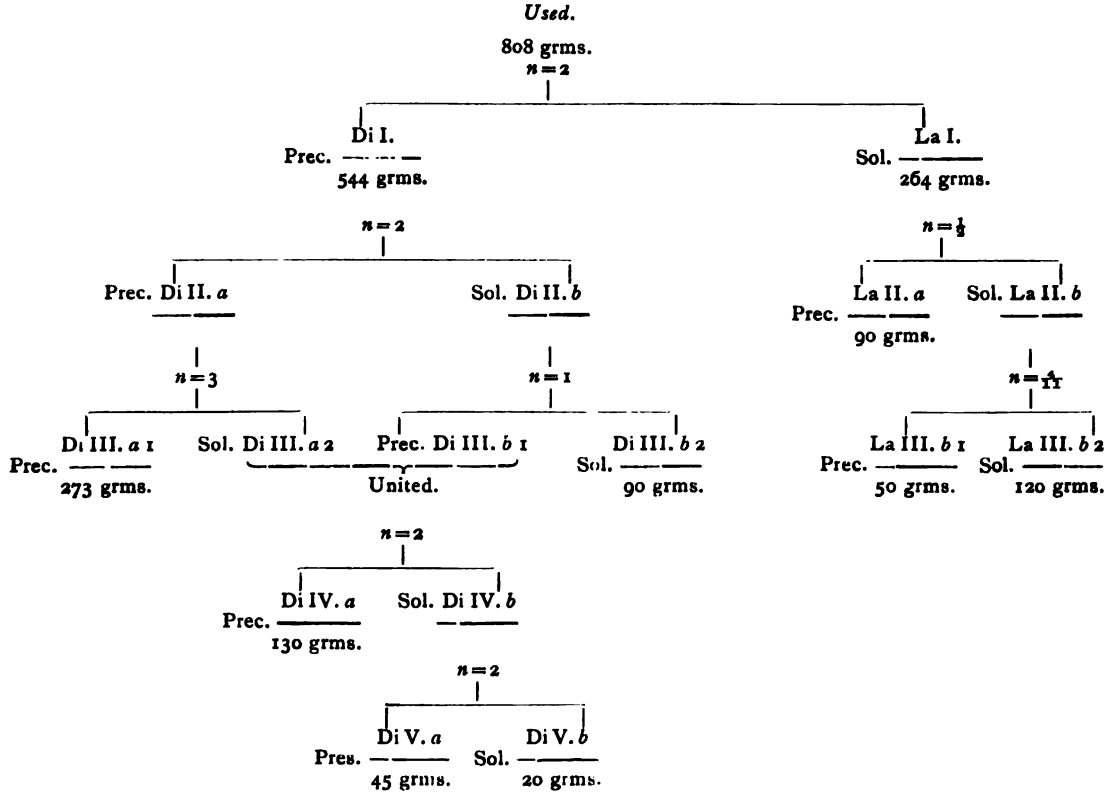
On account of the very tedious and unpleasant work with the above-mentioned, quite amorphous, and rather bulky precipitates of nitrates, no further attempts were made to obtain a salt of lanthanum perfectly free from didymium, and a salt of didymium perfectly free from lanthanum, by this method. The fractions La II. a, Di III. b_2, and Di V. a were, instead, united as almost of equal value, and the six fractions of the total material thus obtained were submitted to the process of crystallising their double nitrates, as it will be briefly explained in the next section.

* *Berichte der Deutsch. Chem. Gesel*

4. *Preparation of a Pure Lanthanum Salt and Partial Re-solution of Didymium into its Components by the Crystallisation of the Double Ammonium Nitrates.*

The principles and the practical execution of this process have been described by Auer von Welsbach with such completeness that we need merely mention in addition a few stratagems which are adapted to expedite the very tedious operation.

The crystallisation may be easily performed in rather deep porcelain capsules of suitable size, in which the saline solution, acidulated with nitric acid, set upon a wire net, and heated with a small flame until minute crystals become visible upon the surface, which do not disappear upon stirring after the removal of the flame. These tiny crystals are not the double salt sought for, $R^{III}(NO_3)_3.2NH_4.NO_3.4H_2O$, which appears in fine massive monosymmetric prisms and tables, but probably a compound poorer in water. When the chief quantity of the lanthanum salt has been fractionated out, it is important that the six or eight fractions to be obtained from each portion of salt should be approximately equal in quantity. In order to effect this without weighings, we add to the hot liquid a little cold water from the washing-bottle, stir up, and place a drop on a watch-glass. We then add by means of forceps with platinum points a trace of the crystallised salt of an approximately equivalent fraction, and stir up with one of the points of the forceps. If too much water had not been added, crystallisation begins immediately in the drop, and is completed in a few seconds. If the entire drop congeals to a paste, a little more water is cautiously dropped into the capsule, and the experiment is repeated in another part of the watch-glass. In this manner with a little practice it is easy, from the quantity of crystals obtained in the drop, to estimate approximately



the quantity obtainable from the entire solution. After the solution has been duly concentrated, some of the crystalline paste on the watch-glass (which may be inspissated at pleasure by heating the watch-glass and crystallising anew) is added to the liquid, which has been allowed to cool in the air, at its margin in small quantities until the formation of crystals is observed; the rest of the crystalline paste is then distributed at two other places of the capsule, covered over, and left to itself from six to twelve hours according to the proportion of saline matter. A more prolonged crystallisation extending to twenty-four hours is requisite only at the beginning when larger quantities of saline matter are concerned. It often happens in the course of the operation that the impurities present, calcium and ferric nitrate, &c., and an excess of ammonium nitrate, accumulate to such an extent that the liquid can no longer be brought to crystallise. The fraction must then be precipitated with oxalic acid, and the oxalate be re-converted into the double salt.

As regards the formation of the simple series of crystals, the above material was treated as follows:—After the saline mass taken in hand was resolved into six to eight portions of crystals of the first series, each of the latter was again severed into five to six portions, so that there resulted some forty fractions. Of these, all those were mixed together which at an approximately equal degree of concentration showed no difference in the tone of their colour if compared in glass vessels of similar form. Thus the number of fractions was reduced to some twenty. Of these, the even numbers were brought to crystallise by crystallising out about half of the saline mass which they held in solution, and then each time adding the mother-liquor to the succeeding but the crystals to the foregoing fraction, after the former has been rinsed in the capsule with a little concentrated nitric acid. The crystals of fraction 2 were thus put to fraction 1, the mother-liquor and the washings to fraction 3; the crystals from fraction 4 to fraction 3, the mother-liquor and the washing acid to fraction 5, &c.

The ten (about) fractions thus obtained were called the second series. By again dividing each of these portions into five or six deposits of crystals, and mixing together the solutions of the same colour, we again obtained some twenty of the latter, which, by using the above halving-process, yielded about ten fractions of the third series, &c. These fractions in each series were then characterised by Roman numerals, the several fractions obtained from splitting up fraction I. as $I._1$, $I._2$, $I._3$; those from II. as $II._1$, $II._2$, $II._3$. . . . When towards the end of the process differences of colour were no longer perceptible, fraction $I._3$ was united to $II._1$, fraction $I._4$ with $II._2$, fraction $I._5$ with $II._3$ and $III._1$, fraction $II._4$ with $III._2$, fraction $II._5$ with $III._3$ and $IV._1$, &c.

Of the saline portions obtained by the oxide process, that produced by the union of three of the mean fractions is separated by a number of crystallisations into portions which have experienced about the same degree of separation as those above characterised, as La III. b_1, La III. b_2, Di IV. a, and Di V. b, and the latter are then united successively with the equivalent fractions of that series. The crystallisation was continued with this material to the eighth and tenth series, and thereby almost all the lanthanum was eliminated mostly as a slightly greenish salt. The didymium fractions were set aside.

Lastly, the didymium main fraction, Di III. a_1, which contained 270 grms. of earths almost free from lanthanum, after conversion into the ammonium double salt, was taken in hand. As, according to Auer von Welsbach, the scission of didymium is more easily effected in presence of lanthanum, this fraction was again mixed with a solution of lanthanum salt of a decided greenish colour containing about 70 grms. of oxide, and the mixture was fractionated by four series of crystallisations. After obtaining the fourth series the lanthanum salt, which had been chiefly recovered in the first fractions, was again distributed among the intermediate and the last fractions, the addition of lanthanum then ceasing.

As it was chiefly important to establish the behaviour of all the earths present in the raw material (excepting the cerium oxides) towards the crystallisation process of the double ammonium nitrates, the separation of the feebly basic earths of the yttrium group by the oxide process was intentionally omitted. On the other hand, the last syrupy and uncrystallisable mother-liquor of the above-mentioned fourth series was precipitated with oxalic acid before the addition of lanthanum, the oxalate was converted into oxide, dissolved in hydrochloric acid, and the solution precipitated with finely powdered potassium sulphate in excess. The precipitate was carefully washed with a saturated solution of potassium sulphate, and decomposed by boiling with a large excess of soda-lye. The flesh-coloured and rather compact hydroxide after washing with hot water was again dissolved in hydrochloric acid, and on precipitation the oxalic acid, &c., yielded 51·6 grms. of earths, to which, after conversion into the ammonium double salt, about 30 grms. lanthanum oxide were added in the form of the greenish double salt. Now crystals were obtained of the normal form, but only in thin lamellæ, which retained the glutinous mother-liquor very obstinately. The crystals were therefore drained, washed with a little concentrated nitric acid, and again further fractionated along with the foregoing fraction, whilst the mother-liquors which contained much lanthanum were set aside as the final fraction.

(To be continued.)

ON THE VALUE AND THE VARIATIONS OF THE CHEMICAL VALENCIES.

By CARLO EMILIO CARBONELLI.

This memoir is reprinted from the *Transactions* of the Ligustic Society of Natural Science (*Società Ligustica di Scienze Naturali*). In it the author seeks to establish the following propositions.

Each element has a characteristic tendency, common in general to the entire Mendeleeffian group to which it belongs, to consist in a fixed number of special atomic groupings which have a different stability according to the nature of the substance.

Compounds may be generated by substitution, by addition, and by substitution along with addition. There exist special groups (radicles) which act as regards their valency like isolated atoms.

Hydroxile exists only in acids and in bodies which, though neutral, like alcohol and H_2O, possess hydrogen capable of substitution. Only the hydrogen of hydroxyl is substitutable by metals; H_2O is, however, a monobasic acid. The anhydrides are not saturated compounds, since they are acids deprived of water.

To form compounds by substitution is a property of the non-metals characterised by the complexity of their molecule.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 237).

I. The Analysis of Cupric Sulphate.

The only published analyses of cupric sulphate which have had for their object the determination of the atomic weight of copper are those previously mentioned. Hampe

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

has very clearly described two extremely concordant electrolytic determinations of the copper contained in the so-called anhydrous salt. The greatest care had been taken to separate minute traces of metallic impurities from the preparation, which had been dried at 250° C.; but apparently it was not realised that for the purpose in hand the retention of a trace of water by the salt was a much more serious possible cause of error than any other. Baubigny's analyses are less fully described, so that it is less easy to judge of their value. A different method, the conversion of cupric sulphate into the oxide by heat, was adopted for these experiments. The result was very different from that obtained by Hampe, but was more nearly accurate, because complicated with a less serious combination of constant errors.

The entire reconciliation of all these results, not only with each other, but also with the more recent analyses, involved the complete analysis and synthesis of cupric sulphate. A somewhat detailed account of the various operations is given below. Many of the less important points are necessarily omitted on account of the already too great accumulation of material, and many relations between the figures can be worked out by those whom they may interest. It is to be hoped that the effort to spare the overburdened literature of to-day any unnecessary additions may not have interfered with the clearness of the description. The first three series of experiments upon the analysis of cupric sulphate constituted a study of the effect of progressive refinement, and the first of the three perhaps hardly deserves a place in a paper on atomic weights. Unless otherwise stated, the data are given in full.

Materials used in the Analysis.

Cupric Sulphate.—The substance used in the first series of experiments was partly prepared from very pure copper remaining from the cupric bromide research, and partly from other sources. It was perfectly neutral and reasonably pure. For the second and third series 400 grms. of the so-called "chemically pure" cupric sulphate of commerce were dissolved in a very large amount of water, and the solution was twice successively treated with a very small amount of potassic hydroxide in dilute solution; the mixture being occasionally shaken and allowed to stand each time for a week before decanting the clear supernatant liquid. One quarter of a grm. of ammonic bromide was added to this liquid; and after standing two weeks the solution was carefully filtered, evaporated to very small bulk in a porcelain dish, and again filtered from the deposited basic salt. The finely divided crystals obtained from this solution by agitation and cooling with ice were drained with a reverse filter (see *Proc. Amer. Acad. Arts Sci.*, xii., 124), re-dissolved in hot water, and repeatedly re-crystallised in platinum vessels. The first three mother liquors were rejected, but the later ones were all combined. After three more re-crystallisations the substance contained in these mother liquors was dissolved in cold water and allowed to crystallise by slow evaporation in pure air. The preparation thus made was used in the second series of analyses.

The crystals obtained by eight successive crystallisations in platinum vessels were dissolved in cold water, and the salt was slowly re-crystallised over sulphuric acid in a vacuum. The substance thus obtained was dissolved in water which had been distilled in a platinum retort, and after standing six days the perfectly clear solution was again brought to crystallisation in a vacuum. These crystals were dried in a platinum dish over partially dehydrated cupric sulphate, and were used for the third series of experiments. The neutrality of each of these preparations was determined as nearly as possible by means of methyl orange, after the manner described in the *Proc. Amer. Acad. Arts Sci.*, xxv., p. 201.

Sodic Carbonate.—As sodic carbonate formed one of the chief bases for the determination of the sulphuric acid, its manufacture in a pure state was a matter of great importance. From the "chemically pure" material of commerce one may easily procure by five re-crystallisations a material which gives no colouration with ammonic sulphydrate, nor, after neutralisation, with potassic sulphocyanide.* Sodic sulphate and chloride are even more readily separated than traces of iron.

Three separate preparations of sodic carbonate were used in the course of the work. For the first series of comparatively crude experiments the solution of ordinary "chemically pure" material, which almost invariably contains a perceptible amount of finely divided solid matter, was after filtration twice re-crystallised in a platinum dish. It was subsequently found advantageous to prevent the clogging of the filter by two or three preliminary re-crystallisations, in the course of which most of the solid matter finds its way into the mother liquor.

The second sample of sodic carbonate was re-crystallised six times after filtration. The vessels, rod, and reverse filter were all of platinum, and water was used which had been distilled in a platinum retort.

Besides all these precautions, several additional ones were taken in the preparation of the purest sample of sodic carbonate designed for the third series. The water used had been distilled four times: first alone, next over potassic permanganate, then over acid potassic sulphate, and finally in a platinum still without the addition of foreign matter. Every precaution was taken to exclude dust and acid fumes, and the sodic carbonate was re-crystallised ten times after filtration. The salt prepared in this way gives an absolutely odourless warm concentrated solution. The second and third samples gave essentially identical results. Each of the three preparations was pure snow-white, whether fused or unfused; each gave a perfectly clear and colourless solution with water; and not even the first gave the least test for hydrochloric or sulphuric acid.

On the other hand, as Stas has already indicated, the most elaborate precautions are unable to free sodic carbonate wholly from traces of silica and a basic oxide, which is probably alumina. The former impurity was determined in the usual manner. The alumina and silica were determined together in new portions of the salt by exact neutralisation with hydrochloric or sulphuric acids, ignition of the evaporated product, and weighing of the insoluble residue. Phenolphthalein was used to determine the neutral point, and hence the insoluble bases present were necessarily precipitated. It is needless to state that the operations were conducted in platinum vessels. Neglecting two determinations which were vitiated by known impurity, the weight of total residue obtained varied from 0·15 to 0·41 m.grm., while the weight of sodic carbonate taken varied from 1·02 to 3·06 grms. The average of twenty determinations showed about thirteen parts of impurity to exist in 100,000 parts of the salt. Silica constituted about 40 per cent of this impurity. The third specimen did not differ essentially from the second on these averages. Owing to the slight solubility of silica in sodic chloride solutions,† the observed amount of this impurity may be slightly too low, but for the present purpose the correction is unimportant. The filter-papers used in this part of the investigation left upon ignition an ash of 0·00004 grm.

(To be continued).

On an Ethylnitrocetone and an Acetylnitrocetone, derivatives of the Camphosulphophenols.—P. Cazeneuve.—The composition given for ethylnitrocetone is $C_9H_{10}(C_2H_5)(NO_2)O$. That for acetylnitrocetone is $C_9H_{10}(C_2H_3O)(NO_2)O$.—*Comptes Rendus*, cxiv., No. 18.

* Stas appears once or twice to have had more difficulty in accomplishing this result. At other times his experience seems to have coincided with that described above. Compare Aronstein's translation (1867), pp. 112, 270, with 275.

† Stas, Aronstein's translation, p. 279. In this place the correction is applied to sodic chloride, but not to the nitrate formed from it.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 21st, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. J. W. Alcock, Central Brewery, 45, Mott Street, Birmingham; Frederick Whiteley, B.A., 20, Dunkerley Street, Oldham.

The following paper was read :—

9. "*Masrite, a New Egyptian Mineral, and the possible Occurrence of a New Element therein.* By H. DROOP RICHMOND and HUSSEIN OFF.

The mineral in question is a variety of fibrous alum, sent to the Khedival Laboratory at Cairo by S. E. Johnson Pacha. From 1 to nearly 4 per cent of cobalt was found in different samples. This being the first occasion on which cobalt has been met with in Egypt, the authors were led to inquire whether the blue colour used in paintings on Egyptian monuments contained that element; They were unable to detect it, however, in the samples they obtained, which owed their colour to compounds of copper and iron.

The mineral is principally interesting on account of the presence in it of a minute quantity of a substance having properties apparently unlike those of any known element, which the authors provisionally term *masrium*, from the Arabic name for Egypt.

From an analysis of the oxalate, on the assumption that it is a bivalent element, the atomic weight of "masrium" is calculated to be 228; and the authors point out that there is a vacant place in the periodic system in the glucinum calcium group for an element having the weight 225. In many of its properties "masrium" resembles glucinum, and the oxalate is analogous to that of calcium.

Masrite has the composition—

$$(Al,Fe)_2O_3\cdot(Ms,Mn,Co,Fe)O\cdot 4SO_3\cdot 20OH_2,$$

the following being the results of the analysis of one of the samples examined :—

Water	40·35
Insoluble matter	2·61
Alumina	10·62
Ferric oxide	1·63
Masric „	0·20
Manganous oxide . ..	2·56
Cobaltous „ . ..	1·02
Ferrous „ . ..	4·23
Sulphuric „ . ..	36·78
	100·00

Ordinary Meeting, May 5th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Percy Targett Adams, Ophthalmic Hospital, Maidstone; Charles Bayliss, Selby Park, near Birmingham; Arthur Sanderson Bleckly, Thelwall Lea, near Warrington; Henry Couldong, H.M. Mint, Bombay, India; Herbert Entwistle, Crosshill Terrace, 476, Padiham Road, Bromley; John Fenton Newall, Marple, and 8, Market Place, Manchester; Charles James Norris, Skipton Grammar School; Ernest Heber Smith, 54, Cambrian View, Chester.

The following were duly elected Fellows of the Society: —Alexander Barratt; Reginald Busby Brown; George Fitz Brown; Frederick William George Blyth; Meredith Wynter Blyth; Arthur Carey; Frank Comyns, B.A.; Joseph Davies; George Price Dodds; Hudson Donaldson; Walter William Duffield; Walter N. Edwards; Henry Ellison; James Fraser, F.R.S.S.A.; Haridas Gorgari, M.A.; Harold F. Hills; Henry Leonard Hinnel, A.M.I.C.E.; John Theodore Hewitt; John H. B. Jenkins; Hubert Edward Lindley; Albert Augustus Lintern, B.Sc.; George Harry Major; William James McKerrow; Ernest E. Milnes; Cresacre George Moore, B.A.; Albert Morris; Joseph Charles Mulrenan; John Northing; Albert Ernest Richardson; Reginald Edensor Stanley Richardson; John Meadows Smith; William Herbert Stables, B.A.; James Stenhouse; George de Roos Thomson; Arthur Trobridge; Arthur Holt Tuer; Thomas Shortridge Tweedie; Cyprian A. Warren; George Isaac James Wells, F.I.C.; Lawrence John de Whalley, B.Sc.

The following extract was read from a letter to Sir Henry Roscoe, written by Prof. Kühne, of Heidelberg, at the request of Professor Bunsen, who is seriously unwell.

Heidelberg, April 21, 1892.

"Bunsen sent for me this morning and commissioned me to ask you to express to the Chemical Society his most sincere and hearty thanks for the much valued Address, the contents of which have gratified him highly.

"As he has always regarded the foundation of the Society, which he well remembers, as an important event of great scientific promise, so now he looks back with particular satisfaction on the fact that he has been a Fellow since its establishment, and that he has been permitted to take part in the work of the Society, especially during its earlier years, by the publication in its *Transactions* of many of his investigations. The allusion of this circumstance in the Address, and the appreciative recognition of his scientific labours which it contains, have been to him especially grateful. To his deep regret he finds himself unable to write, or indeed, to exert any continued mental effort, and he is therefore obliged to deny himself the pleasure of personally expressing his thanks, but begs that you will ask the Society to accept them in this form."

The following papers were read :—

10. "*The Existence of Two Acetaldoximes.*" By WYNDHAM R. DUNSTAN and T. S. DYMOND. (First Notice.)

Acetaldoxime, $CH_3CH:NOH$, has hitherto been regarded as a liquid capable of existing only in one form, attempts to obtain evidence of the existence of an isomeride having failed; last summer, however, the authors observed that it could be crystallised. The crystals, which are acicular and often several inches long, melt at 46·5° (corr.); when they are melted and the resulting liquid is heated to 100—150°, no decomposition occurs, the boiling point (114·5°, corr.) remaining unaltered, but on cooling, it does not crystallise until nearly 35° below the freezing point of the original liquid, that is at about 12° (corr.). On standing at the ordinary temperature the freezing-point of this liquid gradually rises until it reaches 46·5°. The crystals which separate from the liquid at 12° are found to be the original substance melting at 46·5°.

It thus seems probable that acetaldoxime can exist in two isomeric, or possibly polymeric, forms. The authors propose to designate the modification melting at 46·5° *α-acetaldoxime*, whilst that which is liquid at ordinary temperatures they provisionally name *β-acetaldoxime*.

During the past six months they have been investigating the physical and chemical properties of these two modifications with the view to discovering other differences between them, but these experiments are not yet completed. This preliminary account is now given, as they wish to complete the investigation, Franchimont having recently announced that he has observed the crystallisation of acetaldoxime, and is looking for evidence of an isomeride.

Acetaldoxime may be readily prepared by the action of hydroxylamine chlorhydride on aldehyd-ammonia; the

calculated quantities of these substances are mixed together, and the acetaldoxime extracted from the mixture with ether. The ethereal solution is then carefully distilled in the usual manner. An almost theoretical yield is obtained.

11. "*Sulphonic Acids Derived from Anisoils* (*No. I.*)." By G. T. MOODY, D.Sc.

In the course of experiments made in the Central Institution Laboratory to elucidate the manner in which isomeric sulphonic acids are formed from phenols, and especially to determine the character of the influence of the OH group, the author has had occasion to study the action of sulphonating agents on methyl and ethyl phenyl ethers. He finds that, contrary to the statement of Kekulé (*Zeit. fur Chemie*, 1867, 20), and Opl and Lippmann (*Zeit. fur Chemie*, 1869, 470), anisoil and phenetoil afford only parasulphonic acids.

Kahlbaum's pure preparations were employed in the experiments. The anisoil was dried over sodium and carefully distilled. It boiled constantly at 153° (uncorr.), but the first and last portions were collected apart. On shaking 50 grms. of the ether with an equal volume of sulphuric acid at the ordinary temperature, it readily dissolved, heat being evolved; on adding the solution to water, however, part of the anisoil was liberated, showing that, as in the case of phenol, an intermediate compound is formed before the sulphonic acid. The anisoil thus set free was shaken with a further quantity of sulphuric acid at 80°, when complete sulphonation occurrred. The products were separately converted into calcium salt, which, on evaporation of the aqueous solution, was obtained in beautiful, long, shining needles, containing 4 molecular proportions of water. The sodium salt crystallises in short, slender needles, which fall to powder on exposure to the air; the potassium salt was obtained in small scales, very soluble in water. Further quantities of the same calcium salt were obtained on fractional crystallisation of the mother-liquors, but there was no indication of any other product being formed. The sulphochloride crystallises from petroleum spirit in elongated hexagonal plates melting at 40·5°; the sulphonamide melts at 108°. Sulphonation of anisoil with chlorosulphonic acid, either warm or in the cold, gave rise to the same sulphonic acid, and no other was obtained.

Phenetoil, like anisoil, on sulphonation either with sulphuric acid or with chlorosulphonic acid, either warm or in the cold, gave rise to only the para-acid, the barium salt of which has been described by Lippmann. The sodium salt forms well-characterised, flat, slender, and somewhat brittle needles, and is anhydrous; the sulphochloride crystallises from light petroleum in flat, monosymmetric plates, which melt at 39°, the sulphonamide forming well-defined needles which melt at 150°.

12. "*The Formation of Trithionate by the Action of Iodine on a Mixture of Sulphite and Thiosulphate.*" By W. SPRING.

In his paper on the "Inveatigation of the Change proceeding in an Acidified Solution of Sodium Thiosulphate," Colefax (*Chem. Soc. Trans.*, 1892, 181) credits me with having said that trithionate of sodium is produced when iodine acts on a mixture of sodium sulphite and thiosulphate, and further denies that this is the case. ("Spring's statement is not true.")

As already pointed out (*Chem. Zeitung*, xvi., 146), I never performed the experiment described by Colefax; I made use (*Bull. de l'Acad. Roy. de Belgique*, [2], xxxviii., 1874) of potassium, and not of sodium salts; in the abstract of my paper published in the *Transactions* of the German Chemical Society (vii., 1161, 1874, and not 1873, 1108, as stated by Mr. Colefax), it is true that sodium salts are spoken of, but this is an error which is due to the fact that the proofs were not submitted to me for correction. A perusal of my original paper in the *Bull. de l'Acad. Roy. de Belgique* (*loc. cit.*) will at once convince the reader of this fact.

The difference in the behaviour of potassium and sodium salts, arising from the greater instability of the polythionates of sodium, an instability which I had already pointed out in 1874, is very striking. Hence it would appear that the strictures made by Colefax are beside the question.

However, in order to avoid any misunderstanding in future, I trust that I may be permitted to draw attention to the following facts.

Colefax has performed his experiments under modified conditions, not only as regards the substitution of sodium for potassium salts, but also as to the proportion of iodine which he has made use of. In my experiments with potassium salts, the full proportion of iodine was not used, but a much smaller quantity. The equation $K_2SO_3+K_2S_2O_3+I_2=K_2S_3O_6+2KI$ requires less iodine than would be necessary to oxidise the sulphite to sulphate, and the hyposulphite to tetrathionate of sodium.

I have thought it desirable to ascertain whether a suitable modification of the quantity of iodine used would lead to the production of trithionate, notwithstanding the great instability of this compound, as in the case of my experiments with potassium salts, in 1874. This will explain my delay in contradicting the imputations made by Colefax.

50·4 grms. of sodium sulphite, together with 49·6 grms. of sodium thiosulphate, were dissolved in *iced* water so as to avoid the decomposition of the trithionate in the subsequent action. To this solution 25·4 grms. of iodine, that is, half the quantity required for complete oxidation, were added in small portions at a time. The solution was then mixed with alcohol (95°). After a few days, the well-cooled alcoholic liquid deposited a small quantity of crystals containing sodium trithionate, which was identified by suitable tests. The principal product of the action, however, was sodium sulphate.

Nevertheless, I do not contend that the formation of trithionate takes place in accordance with the equation $Na_2S_2O_3+Na_2SO_3+I_2=Na_2S_3O_6+2NaI$.

My researches on polythionates have convinced me that sulphites have the property of desulphurising the tetrathionates, so as to convert them into trithionates. I think, in consequence, that it will be more in accordance with observed facts to admit that the sodium sulphite, which owes its existence to the employment of a reduced quantity of iodine, decomposes the small quantity of sodium tetrathionate produced in the first instance,—

$$Na_2S_4O_6+Na_2SO_3=Na_2S_3O_6+Na_2S_2O_3.$$

This modified interpretation deprives the interaction of the significance which I had attributed to it in 1874 with reference to the constitution of trithionic acid. I believe, however, that it is nearer to the reality.

The statement ascribed to me by Colefax, although I am not responsible for it, seems, in consequence, to be correct. It is, however, indispensable that the experiments should be performed under exactly the same conditions as those under which I operated when dealing with potassium salts.

13. "*The Determination of the Temperature of Steam arising from Boiling Salt Solutions.*" By J. SAKURAI.

The evidence now on record as to the temperature of the steam arising from boiling salt solutions is exceedingly unsatisfactory. Rudberg has maintained that the temperature of such steam is always the same as that of water boiling under the same pressure, but, under the conditions observed in his experiments, the temperature indicated was evidently not that of the steam, but of a film of liquid water condensed upon his thermometer bulb. Müller came to the conclusion that steam at the moment of its formation within a boiling salt solution has only the temperature of 100°, though it is more or less superheated by rising through the hot solution. Not only is this conclusion difficult to accept on theoretical grounds, but the observations on which it is based are by no means of a convincing character, and are not peculiar to salt solutions.

On the other hand, Faraday and Magnus thought they had proved that the temperature of steam escaping from a boiling salt solution is the same, or nearly the same, as that of the solution, but from the manner in which their experiments were conducted, it is not clear that the temperature they observed was really that of the natural steam escaping from a boiling solution. On the contrary, it would appear that what they determined was essentially the temperature of the wall of the vessel around the thermometer and of the steam superheated thereby.

Such being the case, the author has studied the conditions under which the true temperature of steam escaping from a boiling salt solution may be ascertained, and he has devised a method by which this can be readily effected. The result of his observations is, that *the temperature of steam escaping from a boiling salt solution is the same as that of the solution.* The most essential conditions for success are:—

1. The thermometer used in ascertaining the temperature of the steam must be kept from contact with the solution—even the smallest drops thrown up by ebullition.

2. The effect of the cooling of the thermometer by radiation must be rendered insignificant in proportion to the heating up by the steam. This condition is readily fulfilled by rapid renewal of the vapour in contact with the thermometer by the expedient of combining the introduction of steam from without with the boiling of the solution by the lamp. Ebullition alone should suffice, but the practical difficulties in the way prevent such being the case; the boiling would have to be tumultuous to generate much vapour, and in a short time the solution would become too concentrated for the experiment to be continued with convenience. On the other hand, by duly regulating the amount of steam entering from without, and the height of the flame, an abundant supply of steam can be secured, and the temperature of the boiling solution may be maintained constant within a few thousandths of a degree for any length of time.

3. The walls of that part of the vessel which serves as the steam chamber for the thermometer must be sufficiently protected from external cooling, and yet, at the same time, must not be heated to the temperature of the steam. Through the non-observance of the former condition as in Rudberg's experiments, so much of the steam is condensed in keeping the walls at 100° that it is hardly possible to keep enough passing over the thermometer bulb, while if the latter condition is ignored, as in Magnus's experiments, the indications of the thermometer may be illusory.

In the apparatus employed this last condition was secured by protecting the steam chamber with a jacket, through which passed a slow stream of the vapour generated by gentle distillation of somewhat dilute acetic acid. By modifying the degree of dilution any desired temperature, changing only slowly as distillation proceeded, was obtained in the jacket; in this manner condensation of steam upon the thermometer bulb, as well as upon the surrounding walls, was prevented.

A salt solution, whose boiling-point had been approximately determined and known to be higher than that of the dilute acetic acid, was boiled, and a rapid current of steam introduced into the boiling solution from without. The thermometer for ascertaining the temperature of the steam now rose above that in the jacket, and ultimately attained the same temperature as the boiling solution. The following are an example of the results obtained with a solution of calcium chloride.—(See Table).

Temperature of the			Difference.	
Steam.	Solution.	Acetic acid vapour.	(II)—(I).	(I)—(III).
111·2°	112·5°	110·8°	1·3	0·4
111·7	112·5	110·9	0·8	0·8
112·2	112·6	111·1	0·4	1·1
112·5	112·7	111·3	0·2	1·2
112·7	112·9	111·5	0·2	1·2
113·0	113·0	111·6	0·0	1·4
113·1	113·2	111·8	0·1	1·3
113·3	113·3	111·9	0·0	1·4

14. "*Note on an Observation by Gerlach of the Boiling Point of a Solution of Glauber's Salt.*" By J. SAKURAI.

A few years ago G. T. Gerlach (*Zeit. Anal. Chem.*, xxvi., 413) published a paper in which he mentions that steam escaping from a boiling solution of Glauber's salt containing a crystalline magma of the anhydrous salt indicated a temperature of 100°, whilst the liquid is boiling at 82°, or even at 72°. This observation appeared to me so curious and so anomalous that I was induced to repeat his experiments; the results, on the whole, confirmed his observations as to temperatures, but, at the same time, deprived them of all exceptional character. Gerlach describes his experiments in the following words:

"700 grms. of crystallised Glauber's salt were melted in an iron vessel, and kept boiling for some time. The vessel was then removed from the lamp, and the liquid portion of its contents was poured off as completely as possible, whilst the separated anhydrous salt was left in the vessel. The whole was allowed to cool to about 50° before the vessel was again heated. This vessel was now provided with a tin plate cover having two holes, through one of which a thermometer passed, nearly reaching the bottom of the vessel, and through the other a second thermometer, which hung in the steam chamber over the heated crystalline magma.

"The liquid completely boiled at 82° (Die Flussigkeit kam schon bei 82° C. vollständig in's Kochen), whilst the escaping steam showed the temperature of 100°. The temperature of the heated magma rose but very slowly, and only attained a temperature of about 100°, when the mass was almost dry.

"To this almost dry mass I added 100 grms. of crystallised Glauber's salt, which melted on shaking. The crystalline magma now boiled at as low a temperature as 72° C., whilst the steam indicated 100° C." (*Loc. cit.*, 422.)

It is not correct to say that "the liquid completely boils at 82°, whilst the escaping steam has a temperature of 100°," for it is only a wet mass of anhydrous sodium sulphate that is heated. I found that steam in such a case does not uniformly arise from the heated mass, but escapes from a number of channels produced in those portions of it which are in contact with the sides of the vessel, and which are therefore most heated. The central portion of the magma, where the thermometer bulb is placed, is more slowly heated, and hence the fact that while the steam has a temperature of 100°, the wet magma is at a lower temperature.

In the second experiment, in which some crystallised Glauber's salt is added to the heated magma, the temperature of the latter is, for a time, very much lowered, not only because a quantity of a cold substance is introduced, but also because the fusion of the crystallised salt absorbs much heat. The central portions of the mass, therefore, are at as low a temperature as 72° C., whilst the steam which rapidly forms and escapes along the sides of the vessel is at a temperature of 100°. That the latter does not exhibit a higher temperature is easy to understand from the form of the experiment. It is also needless to mention that the temperature of the whole mass soon rises.

Hence Gerlach's observations are erroneous in so far as they imply that a substance can evolve a vapour hotter than itself.

15. "*Chemistry of the Thioureas.* Part II. (A Preliminary Note)." By EMIL A. WERNER.

In a recent number of the *Berichte* (1892, 48) a paper appeared by A. Bertram entitled "Zur Kenntniss des Monophenylthioharnstoffs und der Imidocarbaminthiosaureester," in which an account is given of the com-

pounds produced by the action of methyl and ethyl haloids on *monophenylthiourea*.

After referring to the several German investigators in this particular field of research, the author proceeds to describe his work, under the impression that this is the first instance in which a mono substituted thiourea has been so studied, overlooking a paper of mine published two years ago in the Society's *Transactions* (1890, 283), in which an account is given of the compounds produced by the action of benzyl chloride and allyl bromide on thiourea, and its *monophenyl* and *symmetrical diphenyl* derivatives.

Since then the investigation has been continued, and the study of the action of the alkyl haloids on certain *unsymmetrical di*-substituted and *tri*-substituted derivatives of thiourea has been almost completed.

It was intended to withhold the publication of the results obtained up to the present until this branch of the investigation was rendered complete by a study of the action of the alkyl haloids on the *tetra*-substituted thioureas.

The appearance of Bertram's paper has necessitated the publication of this note, more particularly as he describes the action of methyl iodide on a tri-substituted thiourea, viz., $CS(N{\cdot}Ph{\cdot}Me)(NHPh)$. The bulk of his paper is a confirmation of my work with monophenyl thiourea already referred to, and had he been aware of my paper, the exceedingly roundabout method used by him in estimating the mercaptans produced by the decomposition of his bases would scarcely have been described.

The following is a brief account of the more important compounds obtained during the continuation of my research, the full details of which shall be submitted to the Society at an early date:—

1. *Unsymmetrical diphenyl thiourea*, $CS(NPh_2)NH_2$, produced by molecular rearrangement of diphenylamine thiocyanate.—Small needles from alcohol, m. p. 198°. Solution immediately desulphurised by $AgNO_3{\cdot}2NH_3$. The isolation of this urea completes the series of possible phenylated thioureas.

2. *Diphenyl cyanamide*, $CN{\cdot}NPh_2$, produced by desulphurisation of $CSNPh_2{\cdot}NH_2$.—Large prisms from alcohol, m. p. 73—74°. This compound is isomeric with the diphenyl cyanamide of Weith, m. p. 292°, and with Hofmann's hexaphenylmelamine $[CN{\cdot}N(Ph)_2]_3$, m. p. above 300°.

3. *Benzyl imidodiphenylthiocarbamate*, produced by the action of $C_6H_5{\cdot}CH_2Cl$ on unsymmetrical diphenyl thiourea; m. p. 182—183°.—The base, $C_{20}H_{18}N_2S$, forms pale yellow crystals, m. p. 125°, and has the constitution $C(NPh_2){\cdot}(NH)S{\cdot}CH_2{\cdot}Ph$.

4. *Benzyl diphenyl thiourea*, $CS(NPh{\cdot}CH_2Ph)NHPh$, from phenylthiocarbimide and benzylaniline.—Colourless crystals from alcohol, m. p. 103°. The alcoholic solution is not desulphurised by $AgNO_3{\cdot}2NH_3$, but yields a characteristic silver derivative, $CS{\cdot}NPh{\cdot}CH_2Ph{\cdot}NAgPh$, which melts at 93°, and decomposes with separation of Ag_2S at 150—160°.

5. *Benzyl phenylimidophenylbenzylthiocarbamate*, from benzyl chloride and the preceding thiourea, is a thick liquid which slowly crystallises.—The base, $C_{27}H_{24}N_2S$, is a thick viscid pale yellow liquid with greenish fluorescence.

6. *Unsymmetrical phenylbenzyl thiourea*,—

$$CS(NPh{\cdot}CH_2Ph)NH_2,$$

produced by molecular re-arrangement of benzyl aniline thiocyanate.—It melts at 136·5°; its alcoholic solution is immediately desulphurised by $AgNO_3{\cdot}2NH_3$. The isomeric thiocyanate, $NH{\cdot}PH{\cdot}CH_2Ph{\cdot}HCNS$, melts at 138°.

Research Fund.

A meeting of the Committee will be held in June. Fellows desiring grants are requested to make application to the Secretaries before June 15th.

PHYSICAL SOCIETY.

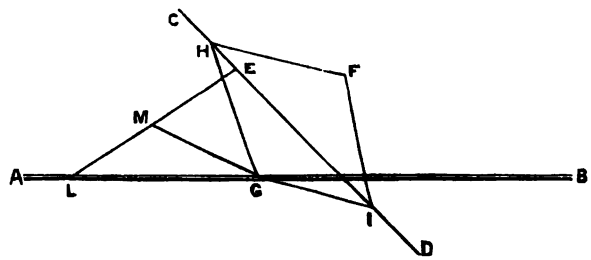
Ordinary Meeting, May 13th, 1892.

Dr. E. ATKINSON, Treasurer, in the Chair.

MR. GERRANS was elected a member of the Society.

Mr. R. INWARDS read a paper on "*An Instrument for Drawing Parabolas.*"

It was designed for drawing curves of short focus, such as are required for reflectors and for diagrams of the paths of comets and projectiles. Its construction is based on the fundamental property that every point on the curve is equidistant from the focus and directrix. In the diagram below, A B is a slot representing the directrix, and F G H I



a rhombus jointed at the corners and pivotted at F, whilst C D indicates a bar capable of sliding through guides at H and I. A rod, L E, is coupled to G by a bar, G M, such that the lengths L M, M E, and M G are equal. As L and G slide along A B the point E describes a parabola whose *latus rectum* depends on the distance of F from A B. In the instrument, F is carried by a slotted arm so that its position is adjustable. G E is always perpendicular to A B and equal to E F.

Prof. BOYS enquired whether the instrument could be modified to draw any conic section by arranging that the ratio of E F to E G, instead of being unity, might be greater or less than unity.

Prof. PERRY said an instrument for drawing curves represented by the equation $y = x^n$ was greatly needed for engineering work.

Mr. F. H. NALDER exhibited and described *Some Electrical Instruments.*

The first shown was a ballistic galvanometer with one pair of coils, the distinguishing features of which were accessibility, small damping, great sensitiveness, and the arrangement of the control. The control is effected by a "tail magnet" carried on a horizontal tube supported by a pillar outside the case, as suggested by Prof. R. M. Walmsley. A small magnet on the cover serves for zero adjustment. The suspended system consists of four bell magnets, two being in the middle of the coil and one at top and bottom respectively, arranged so as to be astatic. The sensitiveness of the instrument shown was such that one-fourth of a micro-coulomb gave 300 divisions (fortieths of an inch) when the periodic time was ten seconds and scale distance about 3 feet. Resistance of galvanometer about 10,000 ohms.

To bring the needle to rest quickly, a damping coil mounted on an adjustable stand, and a special reversing key with resistances in its base, are provided. The key has successive contacts arranged, so that when pressed lightly only a weak current passes round the damping coil, whilst when pressed further a much stronger current flows. The strong currents are used to check the large elongations, and the weak ones for finally bringing to zero.

A lampstand with semi-transparent scale, arranged for use with a glow-lamp, was next shown. Instead of reading by the image of the filament, as ordinarily done, the lantern is arranged to give a bright disc of light with a black line across the middle.

Mr. BLAKESLEY asked if the galvanometer was astatic.

For damping non-astatic ones he had found it useful to wind several turns of wire round the bobbin and put them in series with a few thermoelectric junctions, warmed by the hand, and a key.

In reply, Mr. NALDER said the galvanometer was astatic, but the damping coil could be placed so as to act on one pair of magnets more than on the other.

A paper on "*A Portable Instrument for Measuring Magnetic Fields, with some Observations on the Strength of the Stray Fields of Dynamos*," by E. EDGAR and H. STANSFIELD, was then read.

The instrument was described as an inversion of a d'Arsonval galvanometer, for the torque necessary to maintain a suspended coil conveying a constant current parallel to the field gives a measure of the strength of the field. The constant current is furnished by a Hellensen's dry cell, which the authors found remarkably constant. The instrument consists of a coil of about 50 ohms, wound on mica and suspended by two German silver strips within a tube. A pointer is fixed to the mica and a divided head, to which the outer end of the strip is attached, serves to measure the torsion. Within the head chamber is a commutator which automatically reverses the current in the coil when the head is turned in opposite direction from zero. Two readings may thus be taken to eliminate gravity errors due to want of perfect balance in the coil. Means are provided for adjusting and measuring the tension of the suspensions.

The constant of the instrument was determined by placing the coil in the field of a Helmholtz galvanometer and found to be 0·293 per 1°. Any other field is therefore given by $0{\cdot}293(n+1)\theta$; where θ is the angle of torsion in degrees, and n the multiple of 50 ohms in series with the coil. Fields from two or three C.G.S. lines upwards can be measured to about 2 per cent by the instrument, and even the earth's field is appreciable.

The authors have tested the fields of dynamos at the Crystal Palace Exhibition and elsewhere, and the results obtained are given in the paper. It is noted that the stray fields of multipolar machines fall off much more rapidly than those of the two-pole dynamos as the distances are increased, and that near edges and corners of the magnets the fields are much stronger than near flat surfaces. The disturbing effect of armature reactions on the strength of the stray fields were measured and shapes of the fields observed in some cases. Experiments on magnetised watches are described in the paper.

Mr. WHIPPLE said the Kew Committee were to some extent responsible for the experiments described, for it was on their account that the investigations were commenced. In connection with the rating of so-called non-magnetic watches, it was necessary to know what strength of fields they were likely to be subjected to. The instrument devised for making the tests was a very interesting one, and he results obtained by it of great value.

Mr. A. P. TROTTER hoped the authors would supplement their work by tracing out the directions of the fields of dynamos, and he described a simple method of doing this by a test needle used as an indiarubber stamp. The question of watches, he thought, must be considered soon; even non-magnetic watches were stopped by being placed in strong fields, owing to Foucault currents generated in the moving parts.

Mr. BLAKESLEY inquired whether the instrument could be used in any position. He thought three observations would be necessary to completely determine any field.

Mr. STANSFIELD, in reply, said they used a pilot needle for showing the direction of the fields and then placed the coil accordingly. The instrument could be used in any position, for the weight of the coil was only about 2 grms. and did not greatly alter the tension of the suspensions, which was usually about 300 grms.

A watch with a brass balance was not influenced by a field of 10 C.G.S. lines, but was seriously affected by one of 40.

Mr. JOSEPH W. LOVIBOND read a paper "*On a Unit of Measurement of Light and Colour.*" The paper was illustrated by many coloured charts, diagrams, and models, and several pieces of apparatus by which colour measurements could be made were shown. The principle of the measurements depends on the selective absorption of the constituents of normal white light by coloured glasses (red, yellow, and blue). The depths of tint of the glasses are carefully graduated to give absorptions in numerical proportions. For example, two equal glasses, each called 1-unit red, give the same absorption as a 2-unit red, and so on. The units of red, yellow, and blue are so chosen that a combination of one of each absorb white light without colouring the transmitted light. Such a combination is called a "neutral tint unit." By the use of successive neutral tint units white light can be gradually absorbed without showing traces of colour, and the number of such units required to produce complete absorption is taken as a measure of the intensity or luminosity of the white light.

Methods of representing colours by circles and charts were fully dealt with, and the influence of time of observation on the penetrability of different colours was illustrated by diagrams. The results of 151 experiments on colour mixture were explained and represented diagrammatically.

After the reading of the paper the methods used for colour-matching and measurement were shown by Mr. and Miss LOVIBOND.

Mr. R. W. PAUL exhibited his improved form of Wheatstone bridge arranged to occupy the same space and fulfil the same conditions as the well-known Post Office pattern.

NOTICES OF BOOKS.

Farmyard Manure: its Nature, Composition, and Treatment. By C. M. AIKMAN, B.Sc., F.R.S.E., F.I.C., F.C.S. Edinburgh and London: W. Blackwood and Sons.

THIS treatise, as the author informs us, is essentially a chapter from a work on "Soils and Manures," upon which the author is at present engaged. But brief as it is, it contains much valuable matter. Perhaps at first sight it might be imagined that the author was seeking to controvert the views of Ville and others who have insisted on the value of chemical manures: but on careful reading it will be found that such is not Mr. Aikman's intention. He recognises that farmyard manure contains a very small quantity of the three fertilising ingredients, viz., nitrogen, phosphoric acid, and potash; that these three ingredients are present not in the proportion best suited to the requirements of crops, and that two of these ingredients, nitrogen and phosphoric acid, are found not in their most valuable conditions. Hence he considers that the most valuable properties of farmyard manure must be sought for in its indirect influence. He distinguishes the state in which such manure should be applied respectively on different soils. Thus, on heavy clays he recommends the application of manure in a fresh condition, whilst on light soils it should be used when well rotted. He draws a subtle but very rational distinction between manuring the *soil* and manuring *the crop*. The former procedure, he holds, cannot in these competitive days be believed in, and he strongly doubts whether farmyard manure is economical as compared with chemical manures. He recognises the truth that urine is not a complete manure and must be supplemented by an addition of phosphates. He admits also that farmyard manure contains too little nitrogen in proportion to its mineral constituents, and that it requires reinforcing firstly with nitrogenous matter, and secondly with phosphates.

We cannot find any decided deliverance on the great question whether it is economical—as it is still commonly

done—to raise cattle for the sake of the manure they produce. Ville, it must be remembered, whilst insisting that the excreta of the stock kept on a farm for labour, for meat, milk, &c., should be fully utilised, contends that to keep cattle for the sake of manure is a capital error. His arguments seem convincing, but it would be desirable to see this subject reconsidered under different conditions. Perhaps Mr. Aikman may see his way to a discussion of this subject in his forthcoming large work. In the meantime, the present treatise must be strongly recommended for the general accuracy of its teachings and the clearness and simplicity of its language. There is here assuredly nothing to bewilder the most purely bucolical mind.

CORRESPONDENCE.

THE PROPOSED CHEMICAL BENEVOLENT FUND FOR NECESSITOUS PROFESSIONAL CHEMISTS OR THEIR WIDOWS AND ORPHANS.

To the Editor of the Chemical News.

Sir,—In 1869 the Council of the Institute of Chemistry proposed to found a Benevolent Fund. The response by the Fellows and Associates was insufficient to warrant further action.

Last year I ventured to suggest that the Jubilee of the Chemical Society be in part celebrated by the foundation of a Benevolent Fund open to the claims of any necessitous chemists or of their widows and orphans. The resulting 184 contributions had a capitalised value of over £5000, and were duly offered to the Society. The Council sympathised with the aims of the Fund, and thanked me for my efforts, but announced that the objects of the Chemical Society were, and must continue to be, restricted to the prosecution of Chemical *Science*.

I then asked the contributors if the Fund should be organised on a separate and independent foundation. Almost all replied "Yes."

To ascertain whether or not any fair proportion of the members of the four leading Societies of Professional Chemists in practice in the United Kingdom would support the Fund thus commenced, I issued a printed appeal to each of them (3500). The result was most disheartening. The indifference manifested towards the Institute's project was almost as strikingly shown towards this general Chemical Benevolent Fund. My letters had met with abundant response; these circulars produced very little.

I thank the contributors for their kind interest and aid, but clearly we must cease our endeavours to found a Chemical Benevolent Fund, at all events for the present.

The idea of such a Fund is, however, fast growing, and if a few years hence the leaders in the four Societies would unite in urging the matter, I should have no doubt whatever of a permanently successful result. But in any case the majority of the leaders in these Societies must unitedly lead in contributing to the Fund. Then, and then only, will the followers follow. That is the lesson pressed home to me in my much correspondence on this subject.

I have posted to each contributor a printed statement, which includes the substance of this letter, some memoranda relating to organisation which may be useful at a future time, and a complete list of the promised donations and promised annual subscriptions to a separate and independent Chemical Benevolent Fund. The cheques, unasked for, which were sent to me have been returned in full.—I am, &c.,

John Attfield.

Watford, Herts, May 20, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 18, May 2, 1892.

Novel Case of Abnormal Solution. Saturated Solutions.—F. Parmentier.—The author has shown on a former occasion (*Comptes Rendus*, civ., 686) that in the solution of a solid in a liquid it occurs that if the solid is entirely dissolved it is not possible to obtain, as in known cases, a homogeneous mixture by the addition of any quantity whatever of the solvent. A new instance of this fact is the case of bromised ether in ether $(C_4H_{10}OBr_3)_2$. If to this solid substance there is added ether, it dissolves rapidly; but if we add incressiag quantities of ether there arrives a moment when the excess of ether separates from the liquid produced. As a definition of saturated solutions comprising the various cases of the solution of solids in the liquids the author adopts the following:—When substances can, without combining, yield a homogeneous liquid, the solution is termed saturated, if one of the substances, added in excess to the solution, separates itself from this solution.

Detection of Fluorine in Varieties of Natural Phosphates.—Ad. Carnot.—The author does not indicate any novel or improved method for the recognition and determination of fluorine in phosphates. For apatites he gives the general formula $Ca(F,Cl)+3(PO_53CaO)$, in which a little lime may be replaced by an equivalent quantity of magnesia or of ferrous oxide. The semi-crystalline fibrous phosphorites have almost exactly the composition of crystalline apatites. The earthy or compact and slightly concreted phosphorites contain a smaller proportion of fluorine, and those which are very distinctly concreted with a mamellated surface contain only a slight amount of fluorine, which may sometimes almost be neglected. In almost all the sedimentary phosphates the proportion of fluorine is approximately equal to that in apatites containing an equal amount of phosphate. The author purposes studying the transformation undergone by fossil bones.

The Determination of Small Quantities of Carbon Monoxide by Means of Cuprous Chloride.—L. de Saint-Martin.—This memoir cannot be usefully reproduced without the accompanying figure.

Thermic Study of the Function of Phenol.—M. de Forcrand.—This paper does not admit of abstraction.

Determination of the Surface of Ebullition of the Normal Paraffins.—G. Hinrichs.—This paper requires the two accompanying diagrams.

The Action of Pyridic Bases upon Certain Sulphites.—G. Denigès.—The pyridic bases have little disposition to form compounds with the metallic sulphites. The zinc-pyridine and cadmium-pyridine sulphites alone are well defined, and are sufficiently stable to bear washing and drying without dissociation. The zinc-pyridine sulphite is much more stable than the corresponding cadmium salt.

The Preparation and Physical Properties of Acetyl Fluoride.—Maurice Meslans.—The most advantageous method of preparing this compound consists in causing acetyl-chloride to react upon zinc-fluoride previously dried *in vacuo* at 250°. The product thus obtained is a colourless gas which does not fume in the air. It burns with a blue flame, producing a mixture of watery vapour, carbonic acid, and hydrofluoric acid. Its odour resembles that of carbon oxychloride. If inhaled it produces no immediate action, but in a few minutes it occasions oppression, attended with strong bronchial irritation. In larger quantities it may occasion spitting of blood. Water

dissolves about twenty times its own volume, and then decomposes it slowly. Alcohol, ether, benzene, chloroform, &c., dissolve it in every proportion. It is liquefied at the pressure of the atmosphere at 19·5°.

Diamidosulphobenzide and Some of Its Derivatives.—Ch. Lauth.—Diamidosulphobenzide readily yields diazo-derivatives by the action of a nitrite in presence of hydrochloric acid, and these diazo-compounds, on treatment with the usual reagents, yield fine colouring-matters. Scarlets are obtained with α-sulpho-α-naphthol and disulpho-α-naphthol. These colours, contrary to what might have been hoped, have but little affinity for cotton.

Azo- and Alkyl-Compounds of Chrysaniline, and on the Colouring-Substances derived from them.—A. Trillat and De Raczkowski.—The authors' experiments seem to prove that the azo- and alkyl-derivatives of chrysaniline present but a secondary interest from a tinctorial point of view.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 73.

This issue does not contain any chemical matter.

Bulletin de la Société Chimique de Paris. Series 3, Vols. vii. and viii., No. 8.

This issue contains merely abstracts from other journals.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"The Chemist."—(Reply to J. Cuthbert Welch).—Dr. H. Carrington Bolton's "Catalogue of Scientific Periodicals" (Smithsonian Misc. Col., vol. xxix.), gives on page 155 :—

"The Chemist. . . . Edited by Charles Watt and John Watt. 6 vols. 1840-45.

"Continued under the title—

"The Chemist. . . . Edited by John Higgs Newton. 1 vol. (vii.). 1846-48.

"Continued under the title—

"The Chemist. . . . Edited by John and Charles Watt. New Series. 4 vols. 1849-53.

"Continued under the title—

"The Chemist. . . . Edited by John and Charles Watt. New Series. 5 vols. 1854-58. ‖"

The mark ‖ signifies publication discontinued.—Jas. Lewis Howe, Polytechnic Society of Kentucky, Louisville, Ky., April 26, 1892.

MEETINGS FOR THE WEEK.

Monday, 23rd.—Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Industries," by Percy F. Frankland, F.R.S. (Cantor Lectures).

Tuesday, 24th.—Institute of Civil Engineers, 8.

—— Royal Medical and Chirurgical, 8.30.

—— Photographic, 8.

—— Society of Arts, 8. "The Extension of Colonial Trade," by Colonel Howard Vincent, M.P.

—— Royal Institution, 3. "Some Aspects of Greek Poetry," by Prof. R. C. Jebb.

Wednesday, 25th.—Society of Arts, 8. "Researches in Photochromy," by F. E. Ives.

—— Geological, 8.

Thursday, 26th.—Royal Institution, 3. "On Faust," by R. G. Moulton, M.A.

—— Institute of Electrical Engineers, 8.

Friday, 27th.—Royal Institution, 9. "Emotional Expression," by Sir James Crichton-Browne, M.D., F.R.S.

—— Physical, 5. "On the Present State of Our Knowledge of the Connexion between Ether and Matter—An Historical Summary," by Prof. O. Lodge, F.R.S.

Saturday, 28th.—Royal Institution, 3. "Some Modern Discoveries in Agricultural and Forest Botany," by Prof. H. Marshall Ward, F.R.S.

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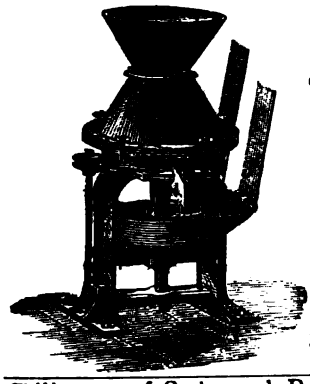

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CONTENTS:—(1) Analytical Processes. (2) Testing for Metals. (3) Testing for Acids. (4) Qualitative Analysis of Simples and Mixtures. (5). Testing for Alkaloids, Poisons, &c. (6) Weighing, Measuring, and Specific Gravity. (7) Volumetric Analysis. (8) Gravimetric Analysis. (9) Ultimate Organic Analysis. (10) Water, Air, and Food. (11) Drugs and Urine. (12) Gas Analysis, &c.

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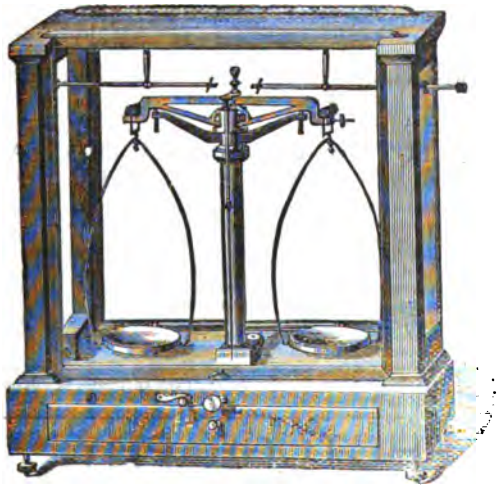

FIG. 32.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1696.

COLOURING-MATTER IN SHELL FISH.

By Dr. JAMES LEICESTER,
Merchant Venturers' Technical School, Bristol.

It is a well-known fact that shrimps and lobsters change colour upon boiling, but the exact cause of this, I believe, is still unknown. The following fact may possibly throw some light upon the subject:—

Take a small flask and place about 100 c.c. of concentrated hydrochloric acid in it; then take three or four shrimps, drop them into the acid, cork the flask, and allow to stand for about four hours. The shrimps, of course, must not have been boiled. Very soon a purple colour is noticed close to the tail, from which place, apparently, the majority of the colouring-pigment appears to come.

After about four hours the whole of the liquid is a bright purple colour resembling litmus solution. This colour goes after three or four days, and the solution becomes of a dirty brown colour.

The colouration is not caused by any iodine compound, but is probably of an organic nature. Acetic acid and caustic potash give slightly yellow solutions.

As soon as enough of this pigment can be isolated, one may be able to ascertain if it is the cause of the bright red colour of the fish after boiling.

3, Queen's Parade, Brandon Hill,
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ON A NEW METHOD FOR THE ESTIMATION OF UNSAPONIFIABLE MATTER IN FATS.

By WILLIAM MANSBRIDGE.

For some years past the ether extraction process has almost universally been employed for the estimation of unsaponifiable matter in fats, and it is now looked upon as the only reliable method.

In spite of its general acceptance, however, it has several drawbacks, of which the most important is, when dealing with some materials, its tediousness. It is often very difficult on this account to obtain concordant results when the analysis is made in duplicate; and even with materials which present least difficulty, sufficient time can seldom be spared if, as in a works' laboratory, several samples have to be examined every day.

The fats most refractory to the ether process are the various qualities of recovered grease and wool-fat, found in commerce under the names of black oil and brown Yorkshire grease.

These bodies contain varying proportions of cholesterin and isocholesterin, together with other alcohols of high molecular weight, of which we have little exact knowledge, and mineral oils from various sources. In addition they may also contain hydrocarbon oils which are not mineral oils, they having been formed in a previous distillation of the oil used for batching the wool. In operating upon such greases, strata intermediate between the soap solution and the ether are formed which effectually prevent the complete separation of the latter; sometimes, indeed, such a perfect emulsion is formed that no separation whatever takes place, rendering it almost impossible to carry the experiment to a satisfactory conclusion.

It being part of my daily work to make a large number of determinations of unsaponifiable matter, and especially in connection with recovered greases, I soon discovered the imperfections of the ether process; and in the hope of finding something better, I have made a large number of experiments with different solvents, and from the material thus accumulated I worked out the following process. I should state here, however, that since I commenced writing this paper I have been made aware that Hönig and Spitz (*Zeit. fur Angew. Chemie*, 1891, 556) in Austria had elaborated and published a process almost identical with this; but as their experiments were almost exclusively carried out on oleines, the present article, dealing with wool-grease and similar bodies, may not be unwelcome as a contribution to the subject.

The solvent which I employ is a fraction of commercial benzoline boiling at 110° F. prepared in the following manner:—Commercial benzoline is distilled in a flask over the water-bath, and the first portion, amounting to about one-fifth of the whole, collected apart; this, when sufficient has been obtained, is re-distilled on the water-bath, in this instance about four-fifths being collected. This should have a boiling-point of 110° F., and should leave no residue on being evaporated; if it fulfil these conditions it may be employed in the analysis. The great advantages of this solvent, which I term "light benzoline," are—its slight solubility in alcohol, permitting a free use of that substance as a washing agent, and its comparatively high boiling-point and consequent slight liability to loss by volatilisation, thus allowing of a higher temperature, which, by rendering the soap solution more fluid, materially assists the separation of the benzoline layer.

In examining a sample I usually take 25 grms. and saponify it in an open basin, or, if considered desirable, under pressure, using alcoholic potash in moderate excess. The soap after boiling with water is decomposed with mineral acid and the fatty acid washed several times with boiling water. By this treatment a mixture of free fatty acids and unsaponifiable matter is obtained. Of this mixture I then take one, two, or four grms., according to the suspected amount of unsaponifiable, arranging the quantity so that about 0·5 grm. is left finally as residue. The portion taken is dissolved in 50 c.c. of methylated spirit, which has previously been saturated with light benzoline, in a conical flask, and 50 c.c. of light benzoline added; the whole is then heated just to boiling under an inverted condenser or a long tube, allowed to cool slightly in order to prevent loss of benzoline, and just neutralised by semi-normal potassic hydrate, the quantity consumed being noted. The contents of the flask are then transferred to a separating funnel, when a very rapid separation of the benzoline carrying the unsaponifiable takes place.

The soapy spirit layer is then removed and 50 c.c. of water at a temperature of 100° F. are added, the whole thoroughly shaken and allowed to stand, when, in cases of a simple admixture of fatty acid and hydrocarbon oil, a very rapid separation takes place; the wash-water is then removed and a further washing with 40 c.c. of warm 70 per cent alcohol is effected. This last completes the removal of traces of soap and also removes water, which, if allowed to remain, would cause objectionable "bumping" in the subsequent distillation. The extraction of the alcoholic soap solution is then repeated and the benzoline washed as before. The two portions may be added and distilled together. Two washings of the alcoholic soap solution have been found sufficient to extract practically all the unsaponifiable matter in any ordinary mixture; crude wool-fat, however, demands a somewhat different treatment. Thus, in dealing with a typical wool-fat, *i.e.*, one containing about 40 per cent cholesterin, &c., I prefer to take 1·0 grm. of the saponified sample, dissolve and neutralise as before, using, however, a rather larger quantity of benzoline. For the first washing I take instead of water the same quantity of 50 per cent alcohol and finish with alcohol as before; four, or even in extreme cases,

five extractions may be necessary, but usually three are sufficient for ordinary accuracy.

As with the ether process, wool-grease of high unsaponifiable content forms intermediate layers of emulsion; but operating as described above I do not find it of sufficient importance to cause much trouble. Should there be, however, any difficulty from this cause, the following manipulation will facilitate the separation:—After shaking up with the first wash-spirit, allow the contents of the separating funnel to rest for about fifteen minutes, then add a few c.c. of nearly boiling alcohol. This so acts on the emulsive layer as to effect an instantaneous liberation of the benzoline; if not quite separated by this treatment more spirit must be added. The wash solutions and spirit should in all cases be reserved for the succeeding extractions, a little of the benzoline being always retained by them, and which, by their being employed over again, is deprived of its unsaponifiable.

The intermediate stratum appears to consist of a slightly soluble soap of a fatty acid having a very high molecular weight. It has recently been examined by J. Lewkowitsch, who found a fatty acid, or mixture of fatty acids, having a high molecular weight.

My own experiments on this subject are confirmatory of those obtained by Dr. Lewkowitsch. This soap forms with the water an emulsion, in which the ascending bubbles of ether, and to a less extent the benzoline, become entangled and effectually retained, sometimes evincing no tendency to separate even after being left for several days.

Many experiments have been made with the view of preventing the difficulty caused by this soapy layer, but, except in the case of warm alcohol, without success. Alcohol appears to act partly by dissolving the soap and partly by reason of its higher temperature, which causes the bubbles to burst and thus set free the benzoline. Used in the way described above I have always found alcohol most effectual.

The distillation may be performed over the water-bath in the usual manner. I prefer, however, to conduct it over the blue flame of an ordinary Argand burner, interposing, if necessary, sufficient wire gauze to modify the heat; it will then usually be found that at the end of the distillation sufficient heat remains in the flask to finish the driving off of the benzoline, which may safely be accomplished by blowing into the warm flask while it is slowly rotated. It is very desirable that the final "drying" should be performed as expeditiously as possible, otherwise large quantities of the unsaponifiable matter may be driven off with the benzoline. Of course, if the unsaponifiable should be very volatile, the distillation must be conducted over the water-bath; suitable precautions should also be observed in the preliminary saponifications.

I have found the method of "drying" over the argand to give results much more accurate than are usually obtained by heating on the water-bath. It is well known that mineral oils, even those of high specific gravity and boiling-point, lose a considerable proportion of their weight if they are retained at comparatively low temperatures for long periods of time, and if they are exposed in thin films the loss is relatively very great; thus if the small amount of ether extract, which in the majority of cases consists entirely of mineral oil, is kept at the temperature of the water-bath for an hour it may lose sufficient to make a difference of 2 to 3 per cent in the calculation of the results.

This objection does not apply to the use of the Argand burner as described above, as is shown by the following experiments:—About 0·5 grm. of pure mineral oil of various specific gravities was introduced to the distillation flask, benzoline was added in the same quantity as was used for the extraction, and the distillation conducted precisely as described for actual analysis; the residue was weighed, and the flask transferred to the water-bath, and again weighed at intervals of ½, 1½, and 3 hours, with the following results:—

I.—*Scotch Mineral Oil* (Specific Gravity 0·885).

Quantity taken	0·612 grm.
1st weighing after distillation on Argand	0·612 „
After ½ hour on water-bath	0·597 „
After 1½ hours on water-bath	0·585 „
„ 3 „ „ „	0·584 „

Loss after 3 hours' heating on water-bath = 4·248 p.c.

II.—*American Mineral Oil* (Specific Gravity 0·896).

Quantity taken	0·620
After distillation and weighing on Argand	0·619
After ½ hour on water-bath	0·614
After 1½ hours on water-bath	0·609
„ 3 „ „ „	0·603

Loss after 3 hours' heating on water-bath = 2·743 p.c.

The process has been employed constantly for the last nine months in the laboratory, where the author is engaged, always with satisfactory results. The residues have occasionally been examined for soap, but only on rare occasions has any been detected, and then only in slight traces.

The accompanying results are adduced as showing the accuracy attainable; they are representative, not having been in any way selected.

1. *Pure Wool-Fat.*—These samples were typical Yorkshire brown greases, containing about 25 per cent of free fatty acids; the remainder, with the exception of 2 or 3 per cent, being cholesterin ethers of stearic, palmitic, and oleic acids. They were treated exactly as above described for wool-fat; an intermediate stratum was formed but did not render any difficulty.

	Unsap. by Extraction.	By Titration.
(i.) Wool-fat ..	29·05 per cent	39·36
Duplicate..	29·25 „	—

	Unsap. by Extraction.	By Titration.
(ii.) Wool-fat ..	41·70	46·79
Duplicate..	41·70	—

2. *West of England Recovered Grease.*—This is a grease recovered from wool-washing, which contains about 60 per cent free fatty acids, the remainder being cholesterin ethers; it may be classed as a semi-wool-fat. It presents the same difficulties to the extraction as the pure wool-fat.

	Unsap. by Extraction.	By Titration.
(i.) West of England grease ..	21·55	23·16
Duplicate	21·05	23·16

	Unsap. by Extraction.	By Titration.
(ii.)	22·81	23·63

3. *Distilled Wool-Fat.*—No. 1, (ii.), after distillation with superheated steam. By distillation a large proportion of the cholesterin and similar bodies is broken up into hydrocarbon oils, which by their presence cause an easier and more complete separation of the benzoline; the intermediate stratum in this case was very slight.

	By Extraction.	By Titration.
(i.) Distilled wool-fat, No. 1, (ii.)..	52·25	48·64
Duplicate	51·90	48·64

4. *Oleine from Distilled Wool-Fat.*—This is the fluid portion of the fatty acids separated by pressure from the solid acids (stearine).

	Unsap. by Extraction.	By Titration.
(i.)	44·35	44·31
Duplicate ..	44·25	—
(ii.)	50·25	47·13
Duplicate ..	50·35	—

The benzoline layer from these analyses and from No. 3, was washed with water, no intermediate layer was formed, and quick and perfect separation took place.

5. *Black Recovered Grease.*—These are greases of low quality which have been scoured from shoddy, &c. They contain about 5 per cent of cholesterin ethers, usually a large quantity of mineral oils varying from 20 to 45 per cent, the remainder being free fatty acids; they do not form such obstinate intermediate strata as wool-fat, and may be examined as described in the first section of the process. The benzoline layer often separates rapidly and completely, and their analysis is easily accomplished.

	Unsap. by Extraction.	By Titration.
Black recovered grease ..	22·61	25·55
Duplicate	22·72	—

It will be seen from the above results that except in the case of pure wool-fat there is a tolerably close agreement between the results obtained by this process and those arrived at by titration (expressed in terms of oleic acid, 282), thus indicating that for practical purposes simple titration, even with unknown greases of low quality, is a near approximation to the real contents of unsaponifiable matter; the difference is certainly not greater than is usually found between the reports of different analysts when the ether process is employed. In the case of pure wool-fats my experience has shown that there is a tolerably constant relation between the results obtained by extraction with benzoline and the titration values, such relation depending on the amount of cholesterin and similar bodies in the grease. The connection is sufficiently constant to allow of its use for determining the presence of mineral oil or resin oil in wool-fat, and thus give a valuable indication as to the purity or otherwise of the sample.

RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

(Concluded from p. 244).

THE crystallisation is continued as far as the eighth series, the last (usually small) portions of the mother-liquor of each series and the last mother-liquor of the ninth series being added to the ultimate fraction, and thus everything non-crystallisable is removed from the main material. Hereupon the fractions of Series 8 were united with the above-mentioned fractions of didymium, which had been set aside, and the crystallisation was continued as far as Series 14.

Here it appeared that by no means only those constituents of didymium to which Auer von Welsbach has given the name praseodymium pass over into the first lanthaniferous fractions, but at the same time also very noticeable quantities of those which form the more readily soluble double ammonium nitrates. In order, therefore, to carry the separation as far as possible, it is not sufficient to remove all the lanthanum from the first green didymium fractions, but a very large number of crystallisations must be carried on in order to transport these more readily soluble constituents to the corresponding fractions at the end of the series.

The bulk of the green lanthanum salts obtained was separately further fractionated for complete purification, and yielded finally two main fractions, La fraction I. containing 119 grms. lanthanum oxide, and La fraction II. with 152 grms. These two fractions, almost saturated solutions of the ammonium double nitrates, when examined with the spectroscope showed no trace of absorption bands in strata of 12 to 15 c.m. in thickness, but nevertheless contained traces of praseodymium, since the lanthanum oxide obtained from both had a slight reddish cast, and as the La fraction I. was almost entirely, and the La fraction II. in part, submitted again to a fractionated crystallisation of the ammonium double salts, and the last mother-liquors were concentrated down to 1 or 2 c.c. and again examined with the spectroscope, faint indications of the three praseodymium bands were recognised in the blue and the violet.

Upon these two fractions there followed six smaller fractions, in which the green colouration appeared constantly stronger and more distinct.

Of the didymium fractions the earliest green ones, up to the twenty-first and twenty-second series, and the following intermediate fractions were further fractionated even up to the twenty-fifth series; with the mean and last fractions the process was continued only to the fifteenth and sixteenth series.

In order to effect the completest possible separation of the crystallisable and the non-crystallisable constituents, the last mother-liquors from the tenth series were not taken directly to the final fraction, but were first collected into two transition fractions. Of these the first was recrystallised twice, the two last mother-liquors were added to the second fraction; the second fraction was then similarly twice re-crystallised, and the two resulting mother-liquors were united to the final fraction. The pure crystals of the first transition fraction, corresponding to about 12 grms. of oxide, and those of the second representing about 20 grms. of oxide, were preserved separately.

After nearly 3000 crystallisations had been carried out (including the crystallisations of the lanthanum fractions), the entire residual didymium material yielded twenty-three fractions, in which lanthanum could be supposed as present only in the three first. The absorption spectra of these twenty-three fractions and of the final fraction will be fully discussed in the second treatise.

* *Berichte der Deutsch. Chem. Gesel*

THE SOLUBILITY OF VARIOUS INORGANIC SALTS IN ACETONE AND OF ACETONE IN DEXTROSE SOLUTIONS.*

By W. H. KRUG and K. P. McELROY.

WE have investigated the solubility of some inorganic salts in acetone, the results being embodied in the following tables:—

Chlorides.	
Sodium chloride..	Insoluble.
Potassium chloride	,,
Ammonium chloride	,,
Calcium chloride	Very sparingly soluble.
Barium chloride	,, ,,
Strontium chloride (anhydrous)	,, ,,
Ferric chloride	Freely soluble.
Zinc chloride (in sticks)	,, ,,
Cobaltous chloride (anhydrous)	,, ,,
Nickelous chloride (anhydrous)	Insoluble.
Cadmium chloride (anhydrous)	Somewhat soluble.
Mercuric chloride	Very freely soluble.
Mercurous chlorides	Insoluble.
Bromides.	
Potassium bromide	Slightly soluble.
Sodium bromide	,, ,,
Cadmium bromide (anhydrous)	Freely soluble.
Iodides.	
Potassium iodide..	Soluble.
Mercuric iodide	,,

* Read before the Washington Chemical Society, March 10, 1892. From the *Journal of Analytical and Applied Chemistry*, vi., No. 4.

Cyanides and Sulphocyanides.

Mercuric cyanide	Freely soluble.
Potassium sulphocyanide	" "
Ammonium sulphocyanide	" "
Ferric sulphocyanide	Soluble.
Cobaltous sulphocyanide	"
Nickelous sulphocyanide	Insoluble.

Nitrate and Nitrites.

Sodium nitrate	Very slightly soluble.
Potassium nitrate	" "
Ammonium nitrate	Slightly soluble.
Barium nitrate	Insoluble.
Bismuth nitrate	"
Lead nitrate	Very slightly soluble.
Silver nitrate	Soluble.
Potassium nitrate	Very slightly soluble.

Carbonates.

Potassium carbonate	Insoluble.
Sodium carbonate (anhydrous)	"

Sulphates and Sulphites.

Copper sulphate (anhydrous)	Insoluble.
Potassium sulphate	"
Ferric sulphate (anhydrous)	"
Ferrous ammonium sulphate (crystalline)	"
Ferrous sulphate (anhydrous)	"
Calcium sulphite	"

Acetates.

Zinc acetate (crystalline)	Soluble.
Copper acetate (crystalline)	Slightly soluble.
Lead acetate (crystalline)	" "
Magnesium acetate	Insoluble.
Sodium acetate	"
Calcium acetate	"

Miscellaneous.

Potassium ferricyanide	Insoluble.
Boric acid	Freely soluble.
Mercuric sulphide	Insoluble.
Potassium chlorate	Very slightly soluble.
Ferric pyrophosphate	Insoluble.
Ammonium molybdate	"
Ammonium oxalate	"
Ammonium tartrate	"
Cupric chloride (crystalline)	Freely soluble.
Nickelous sulphate (crystalline)	Very sparingly soluble.
Lithium chloride (crystalline)	Soluble.
Cobaltous nitrate (crystalline)	Freely soluble.
Nickelous nitrate (crystalline)	Sparingly soluble.
Malic acid	Freely soluble.
Tartaric acid	" "
Oxalic acid	" "

The solubility at 25° C. has been determined quantitatively for the following:—

Substance.	100 parts acetone by weight dissolve—
Potassium iodide	2·930
Potassium bromide	0·023
Mercuric chloride	50·990
Mercuric iodide	2·090
Cobaltous chloride (anhydrous)	8·620

The behaviour of acetone with dextrose solutions is similar to that with sugar solutions. The solubility of acetone in dextrose solutions, ranging from 10 to 50 per cent, was determined for 25° C. The method used was the same as that applied to determine the solubility of acetone in sugar solutions.

100 Grms. Dextrose Solutions Dissolve at 25° C.

Per cent dextrose.	Grms. acetone.
10	747·86
20	237·71
30	146·30
40	72·72
50	32·70

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, May 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, the whole were found to be clear, bright, and well filtered.

The satisfactory condition of the water supply to the Metropolis exhibited throughout the preceding months of the year has been more than maintained during the past month. But in respect to the results indicative of the nearly always minute proportion of organic matter present in the water, so long as the figures continue low, too much stress must not be laid on their monthly or even weekly variations. According to the more or less favourable meteorological conditions affecting the river from time to time, these figures will vary more or less, and have, during the past month, proved to be exceptionally low.

Thus, taking the Thames-derived water for comparison—and a similar result is apparent in the case of the New River and East London Companies' supplies—the mean amount of organic carbon present in the April supply was only 0·125 part in 100,000 parts of the water, as against a mean for the January supply of 0·158 part, and a mean for the first three months of the year of 0·146 part in 100,000 parts of the water.

But even as between the January and April supplies, the difference in the mean proportions of organic carbon present, or 0·033 part in 100,000 parts, is quite immaterial, corresponding as it does to about the one-seventeenth part of a grain of organic matter in a gallon (*i.e.*, 70,000 grains) of the water.

A comparison, in the case of the Thames-derived supplies, of the results obtained during the past month, and the mean results afforded by the previous three months, is given below, but the notably low figures furnished by the past month's supply one can scarcely expect to be continuously maintained:—

	Ratio of brown to blue tint. Means.	Oxygen required for oxidation. Means.	Organic carbon per 100,000. Means.	Organic carbon per 100,000. Maxima.
First three months	9·8 : 20	0·045	0·146	0·204
April ..	5·6 : 20	0·033	0·125	0·147

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

AN ALLEGED NEW ELEMENT.

THE *Chemiker Zeitung* gives the following particulars concerning masrium, a supposed new element obtained from an Egyptian mineral:—This mineral, found by Johnson Pasha in 1890, was known at first as Johnsonite, but has since been re-named masrite. Richmond and Off found in this mineral cobalt, which attracted attention, as no Egyptian ore of this metal was yet known. A large sample of the mineral (150 kilos.) was conveyed to the Government Laboratory, and was found to contain—

Water	40·39
Alumina	10·62
Ferric oxide	1·63
Masrium oxide	0·20
Manganous oxide	2·56
Cobalt oxide	1·02
Ferrous oxide	4·23
Sulphuric acid	36·78

The mineral was dissolved in water and precipitated with hydrogen sulphide in an acetic solution. In place of the black cobalt sulphide there fell at first a white precipitate, which was allowed to subside. From it, after a somewhat circumstantial treatment, an approximately pure hydroxide was obtained. The atomic weight of masrium was determined as 228. It forms only one oxide, MsO, a white substance. The sulphate, $MsSO_48H_2O$, is a white salt, which crystallises badly from water, but readily from a 50 per cent alcohol. It forms an alum and a double salt with potassium sulphate.

The reactions of masrium are:—Hydrochloric acid produces no precipitation; sulphuretted hydrogen gives no precipitate in presence of hydrochloric acid, but a white precipitate in presence of acetic acid. Ammonia throws down white masrium hydroxide insoluble in excess. Ammonium sulphide and ammonium carbonate give white gelatinous precipitates insoluble in excess of the precipitant and in ammonia. Ammonium phosphate gives a white precipitate insoluble in excess of phosphate and in ammonia. Caustic alkalies give a white precipitate soluble in excess. Potassium ferrocyanide gives a white precipitate insoluble in excess of ferrocyanide and in dilute hydrochloric acid, but soluble in excess of masrium chloride. Ferricyanide gives no precipitate. Ammonium acetate give a precipitate in a boiling solution of masrium, which re-dissolves on cooling. Potassium chromate gives a yellow precipitate soluble in excess of masrium chloride. Potassium tartrate gives a white precipitate soluble in excess. The free metal has not been obtained, neither has any vapour density been determined nor spectroscopic examination effected.

(There is evidently here need for verification and further investigation).

Constitution of the Carbide Derivative of Perseite.—L. Maquenne.—The xylene hydrides, C_8H_{16}, derived from camphoric acid yield with bromine and aluminium chloride the same reaction as toluene hexahydride. It is the same with the naphthenes.—*Comptes Rendus*, cxiv., No. 9.

METHODS FOR THE DETERMINATION OF NITROGEN.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

THE ABSOLUTE OR CUPRIC OXIDE METHOD.

(Applicable to all nitrogen determinations).

THE apparatus and reagents needed are as follows:—

Apparatus.

Combustion tube of best hard Bohemian glass, about 26 inches long and ½ inch internal diameter.

Azotometer of at least 100 c.c. capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing-paper.

Reagents.

Cupric Oxide (coarse).—Wire form; to be ignited and cooled before using.

Fine Cupric Oxide.—Prepared by pounding ordinary cupric oxide in mortar.

Metallic Copper.—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

Sodium Bicarbonate.—Free from organic matter.

Caustic Potash Solution.—Dissolve commercial stick potash in less than its weight of water so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt, solution must be discarded.

Loading Tube.

Of ordinary commercial fertilisers take 1—2 grms. for analysis. In the case of highly nitrogenic substances the amount to be taken must be regulated by the amount of nitrogen estimated to be present. Fill tube as follows: (1) about 2 inches of coarse cupric oxide. (2) Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analysed, about 4 inches of the tube; pour on this the substance, rinsing watch-glass with a little of the fine oxide, and mix thoroughly with spatula; pour into tube, rinsing the scoop with a little fine oxide. (3) About 12 inches of coarse cupric oxide. (4) About 3 inches of metallic copper. (5) About 2½ inches of coarse cupric oxide (anterior layer). (6) Small plug of asbestos. (7) Eight-tenths to 1 grm. of sodium bicarbonate. (8) Large loose plug of asbestos; place tube in furnace, leaving about 1 inch of it projecting; connect with pump by rubber stopper smeared with glycerin, taking care to make connection perfectly tight.

Operation.

Exhaust air from tube by means of pump. When a vacuum has been obtained allow flow of mercury to continue, light gas under that part of the tube containing metallic copper, anterior layer of cupric oxide (see 5th above) and bicarbonate of soda. As soon as vacuum is destroyed, and apparatus filled with carbonic acid gas, shut off the flow of mercury, and at once introduce the delivery tube of the pump into the receiving arm of the azotometer, and just below the surface of the mercury seal of the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture that may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet at a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at rate of about one per second or a little faster.

When the jets under mixture have all been turned on light jets under layer of oxide at end of tube. When evolution of gas has ceased, turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury, and extinguish lights. Allow azotometer to stand for at least an hour, or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer, note volume of gas, temperature, and height of barometer; make calculations as usual. The labour of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Raleigh, N.C.).

The above details are, with some modifications, those given in the report of the Connecticut Station for 1879 (p. 124), which may be consulted for details of apparatus, should such details be desired.

The Kjeldahl Method.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

1. Standard hydrochloric acid whose absolute strength has been determined:—(*a*) By precipitating with silver nitrate and weighing the silver chloride as described in Crookes's "Select Methods," p. 571; (*b*) by potassium tetra-oxalate which has been purified by re-crystallising two or three times; (*c*) by determining the amount neutralised by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate. Half normal acid, *i.e.*, containing 18·23 grms. hydrochloric acid to the litre, is recommended. Cochineal or dimethyl-aniline orange to be used as the indicator in standardising the acid.

2. Standard ammonia, whose strength, relative to the acid, has been accurately determined. One-tenth normal ammonia, *i.e.*, containing 0·7 grm. ammonia to the litre, is recommended for accurate work.

3. "C. P." sulphuric acid, specific gravity 1·83, free from nitrates and also from ammonia sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen. Eimer and Amend's "Strictly C. P." is good.

4. Metallic mercury or mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate cannot safely be used.

5. Potassium permanganate tolerably finely pulverised.

6. Granulated zinc, pumice stone, or one-half grm. of zinc dust to be added to the contents of the flasks in distillation, when found necessary in order to keep from bumping.

7. A solution of 40 grms. of commercial potassium sulphide in 1 litre of water.

8. A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the colour of the product. That of the Greenbank Alkali Company is of good quality.

9. Solution of cochineal prepared according to Fresenius's "Quantitative Analysis," second American edition, p. 679.

10. Kjeldahl's digestion flasks of hard, moderately thick, well-annealed glass. These flasks are about nine inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225—250 c.c.

11. Distillation flasks of ordinary shape, of 550 c.c. capacity, or preferably flasks of the same capacity, of pear-shaped bottom, of well-annealed glass, for both digestion and distillation, and fitted with a rubber stopper and a bulb tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs are about 1½ inches in diameter, the tubes being the same diameter as the condenser, and cut off obliquely at the lower end. This is adjusted to the tube of the condenser by a rubber tube.

12. *A Condenser.*—Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block-tin. The upper ends of the tin tubes should be bent so that the glass connections may have a slope toward the distilling flasks. All kinds of glass are decomposed by steam and ammonia vapour, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, *Ber. Berichte*, xvii., p. 34). The condenser in use in the laboratory of the Connecticut Experiment Station, devised by Prof. Johnson, consists of a copper tank, supported by a wooden frame, so that its bottom is 11 inches above the work-bench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to 6 inches. It is provided with a water-supply tube which goes to the bottom, and a larger overflow pipe above. The block-tin condensing tubes, whose external diameter is three-eighths of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1½ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into precipitating beakers or Erlenmeyer flasks of about 300 c.c. capacity. The titration can be made directly in them. The distillation flasks are supported on a sheet-iron shelf, attached to the wooden frame that supports the tanks in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze or asbestos under the flask, and three other lips, which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stop-cock like those of a gas-combustion furnace. These burners are of a larger diameter at the top, which prevents smoking when covered with fine gauze to prevent the flame from striking back.

13. The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as long as the pan, 5 inches wide and 4 inches high. In this are cut six holes 1½ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. With a little care the naked flame can be applied directly to the flask without danger.

The Determination.

1. *The Digestion.*—Seven-tenths to 2·8 grms. of the substance to be analysed, according to its proportion of nitrogen, is brought into a digestion flask with approximately 0·7 grm. of mercuric oxide, or its equivalent in metallic mercury, and 20 c.c. of sulphuric acid. The flask is placed on the frame above described, in an inclined position, and heated below the boiling-point of the acid for from five to fifteen minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils briskly. No further attention is required till the contents of the flask have become a clear liquid, which is colourless, or at least has only a very pale straw colour. The flask is then removed from the frame, held upright, and while still hot, potassium

permanganate is dropped in carefully and in small quantity at a time till, after shaking, the liquid remains of a green or purple colour.

2. *The Distillation.*—After cooling, the contents of the flask are transferred to the distilling flask with about 200 c.c. of water, and to this a few pieces of granulated zinc, pumice stone, or one-half grm. of zinc dust when found necessary to keep the contents of the flask from bumping, and 25 c.c. of potassium sulphide solution are added, shaking the flask to mix its contents. Next add 50 c.c. of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all of the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in cases of substance most difficult to oxidise, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercuro-ammonium compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen, and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

*Kjeldahl Method Modified to Include the Nitrogen of Nitrates.**

(Applicable to all fertilisers containing nitrates).

Besides the reagents and apparatus given under the Kjeldahl method there will be needed—

1. Zinc dust. This should be an impalpable powder; granulated zinc or zinc filings will not answer.
2. Zinc sulphide.
3. Commercial salicylic acid.

The Determination.

Bring from 0·7 to 1·4 grm. of the substance to be analysed into a Kjeldahl digesting flask, add to this 30 c.c. of sulphuric acid containing 2 grms. of salicylic acid, and shake thoroughly; then add *gradually* 2 grms. of zinc dust, shaking the contents of the flask at the same time, or add to substance 30 c.c. of sulphuric acid containing 1 grm. of salicylic acid; then add direct 2 grms. of zinc sulphide. Finally, place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0·7 grm. mercuric oxide, or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colourless, or nearly so. (In case the contents of the flask are likely to become solid before this point is reached, add 10 c.c. more of sulphuric acid). Complete the oxidation with a little permanganate of potash in the usual way, and proceed with the distillation as described in the Kjeldahl method. The reagents should be tested by blank experiments.

The Ruffle Method.

Apparatus and Reagents.

1. Standard solutions and indicator the same as for the Kjeldahl method.
2. A mixture of equal parts by weight of fine slaked lime and finely powdered crystallised sodium hyposulphite.
3. A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulphur.
4. Granulated soda-lime, as described under the soda-lime method.
5. Combustion tubes of hard Bohemian glass, 20 inches long and ¼ inch in diameter.
6. Bulbed U-tubes or Will's bulbs, as described under the soda-lime method.

Preparation.

1. Clean, and fill the U-tube with 10 c.c. of standard acid.

2. Fit cork and glass connecting tube. Fill the tube as follows:—(1). A loosely fitting plug of asbestos, previously ignited, and then 1 to 1½ inches of the hyposulphite mixture. (2). The weighed portion of the substance to be analysed is intimately mixed with from 5 to 10 grms. of the sugar and sulphur mixture. (3). Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analysed, as previously prepared; mix carefully and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the hyposulphite mixture and pour into the tube; then fill up with soda lime to within 2 inches of the end of the tube. (4). Place another plug of ignited asbestos at the end of the tube and close with a cork. (5). Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Make connection with the U-tube containing the acid, aspirate, and see that the apparatus is tight.

The Combustion.—Place the prepared combustion tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda lime portion until it is brought to full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U-tube begins to recede toward the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker or porcelain basin, add a few drops of the cochineal solution, and titrate.

The Soda Lime Method.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

1. Standard solutions and indicator the same as for the Kjeldahl method.
2. Granulated soda lime, fine enough to pass a 10-mesh sieve, and thoroughly dry.
3. Fine soda lime, fine enough to pass a 20-mesh sieve, also thoroughly dry.

To prepare soda lime of the required fineness, the coarse granulated article of the trade may be ground until it will pass through a sieve of about ten-hundredths inch mesh. It is then sifted on a sieve of about twenty-hundredths inch mesh to separate the fine from the coarse. The two portions are then thoroughly dried in the air bath, or by heating in a porcelain dish or iron pan over a lamp, stirring constantly.

Excellent soda lime may be easily and cheaply prepared according to the directions of Professor Atwater (*Am. Chem. Journal*, ix., p. 312), by slaking 2½ parts of quicklime with a strong solution of 1 part commercial caustic soda (such soda as is used in the Kjeldahl process), care being taken that there is enough water in the solution to

* Described by Prof. M. A. Scovell.

slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and when cold ground and sifted as above.

Instead of soda lime, Johnson's mixture of carbonate of soda and lime or slaked lime may be used.

Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda lime, and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analysed than is the case with soda lime.

4. Asbestos which has been ignited and kept in a glass stoppered bottle.

5. Combustion tubes about 40 c.m. long, and about 12 m.m. internal diameter; drawn out to a point and closed at one end.

6. Large bulbed U-tubes with glass stopcock or Will's tubes with four bulbs.

The Determination.

The substance to be analysed should be powdered fine enough to pass through a sieve of 1 m.m. mesh; 0·7 to 1·4 grms., according to the amount of nitrogen present, is taken for the determination. Into the closed end of the combustion tube put a small loose plug of asbestos, and upon it about 4 c.m. of fine soda lime. In a porcelain dish or mortar mix the substance to be analysed thoroughly, but quickly, with enough fine soda lime to fill about 16 c.m. of the tube, or about 40 times as much soda lime as substance, and put the mixture into the combustion tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda lime, which is to be put in on top of the mixture. Fill the rest of the tube to about 5 c.m. of the end with a granulated lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda lime should be not less than 12 c.m. long. Lastly, put in a plug of asbestos about 2 c.m. long, pressed rather tightly, and wipe out the end of the tube to free it from adhering soda lime.

Connect the tube by means of a well-fitting rubber stopper or cork, with the U-tube or Will's bulbs containing 10 c.c. standard acid, and adjust it in the combustion furnace so that the end projects about 4 c.m. from the furnace, supporting the U-tube or Will's bulb suitably. Heat the portion of the tube containing the granulated soda lime to moderate redness, and when this is attained extend the heat gradually through the portion containing the substance so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly to the same degree. Keep up the heat until gases have ceased bubbling through the acid in the bulbs and the mixture of substance and soda lime has become white or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour, or not more than one hour. Remove the heat, and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion tube.

It is found very advantageous to attach a Bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent "sucking back" in case of a sudden condensation of steam in the bulbs.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 245).

Since the silica and alumina are probably present as sodic silicate and aluminate in the original carbonate, and may be considered as replacing carbon dioxide molecule for molecule, it is evident that the correction to be applied will not equal the whole weight of the residue. Upon this assumption the correction when phenolphthalein is used as an indicator amounts to about half the weight of the impurity, or about 0·007 per cent of the weight of the sodic carbonate. Toward methyl orange aluminic hydroxide is alkaline; hence in this case the errors due to the two impurities tend to counterbalance each other, and the correction may be omitted. The presence of a small amount of alumina thus explains the slight difference observed later between the results obtained with these two indicators.

The crystallised sodic carbonate was dried over pure boiled sulphuric acid in a vacuum, and subsequently ignited to a dull red heat in a double crucible over a Berzelius spirit lamp. The latter apparatus was employed in order to avoid the possible introduction of impurity from illuminating gas. It was found that the salt could be ignited to perfectly constant weight at any temperature between dull redness and its fusing point. The light powder contracts and "sinters together" at a low red heat, and then remains essentially unchanged in weight until it melts. The unfused salt was not observed to gain perceptibly in weight upon an hour's exposure to the air of the balance case; upon the other hand, the fused salt, which of course was never used as a basis of determination, was markedly hygroscopic.

Acids.—The chemically pure hydrochloric and nitric acids were each distilled three times successively in a platinum still. Large quantities evaporated in open dishes left unweighable and scarcely visible residues. The insignificant amount of the residues was a proof of the purity of the air, as well as of the acids. Neither acid gave a test for iron, and the nitric acid contained no chlorine even at the beginning of the operations.

Since the platinum still was very large, it was found more convenient to distil sulphuric acid from a small hard glass retort heated by a ring burner, immediately before it was needed. After three such distillations, a preparation was obtained which left no weighable residue upon the evaporation of any quantity used in the work.

All sulphuric acid used for drying was boiled with ammonic sulphate.

In order to keep the air of the laboratory quite pure, during the greater part of the time neither volatile acids nor ammonia were allowed in the room devoted to the investigation, and all available precautions were taken against dust.

Indicators.—As is well known, the salts of most of the heavier metals are acid toward phenolphthalein and neutral toward methyl orange. The most important consequence of this relation has already been pointed out. When the former indicator was used, the slightly acidified solution was of course first freed from carbonic anhydride by long-continued heating upon the steam bath, and the end point was determined with pure caustic alkali. It is a noteworthy fact that methyl orange is useless in very concentrated solutions of sodic sulphate, the colour change becoming apparent only upon dilution. This indicator is naturally less serviceable in the presence of a strong colour like that of a copper salt. It is less sensitive with cupric sulphate than with cupric bromide. In such cases as these, colorimetric comparison can alone

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

afford accurate results; but even here the effect of a personal equation must be more or less perceptible.

Since the amount of either indicator used in any one case was not more than the thirtieth of a milligrm., it could not have seriously influenced subsequent operations with the solution.

Water.—The distilled water taken hot from the tin-lined condenser around a steam drying oven contained no ammonia discoverable by Nessler's reagent, and in the first crude experiments this water was used without further treatment. After having been once more distilled in a platinum still, it appeared to be very pure. The first portions of the distillate were rejected, although no ammonia was found in them. The water left absolutely no trace of residue upon evaporation, even after long standing. Such doubly distilled water was used in the second series of experiments.

For the third series all the water used, even for minor operations, was distilled four times: first alone, then over alkaline potassic permanganate, next over acid potassic sulphate, and finally once more alone in the platinum still. Since this water was not different in any of its properties from the second preparation, the last refinements were probably unnecessary; and in later work water which had been distilled only twice was used.

The value of the present work has been largely increased by the unlimited supply of platinum ware placed at the disposal of the writer through the kindness of Professor Cooke. Because of the large size of some of the retorts and bottles, it was impossible to free these vessels from iron after the method of Stas. Accordingly they were digested alternately with strong hydrochloric and nitric acids until pure acid which had remained in them for days gave no test for iron after evaporation on the steam bath.

Smaller vessels were freed from iron in the usual manner, by treatment with the vapours of ammonic chloride at a red heat, as well as with fused acid potassic sulphate. They were usually protected during ignition by an outer crucible, from which they were separated by a coil of platinum wire. Crucibles weighing 20 grms. rarely showed a variation of more than one-twentieth of a milligrm. between the weights taken before and after any ordinary operations, excepting when ignited with cupric oxide under conditions which will be explained later.

(To be continued).

NOTICES OF BOOKS.

Fuels: Solid, Liquid, and Gaseous. Their Analysis and Valuation. For the Use of Chemists and Engineers. By H. Joshua Phillips, F.I.C., F.C.S. Second Edition, Revised and Enlarged. London: Crosby Lockwood and Son.

The rise in the price of coal due to the action of parties hostile to each other, but jointly hostile to the public and to the industrial world, renders attention to its economic utilisation a matter of the foremost importance. Hence, such a work as the present deserves and will doubtless receive the appreciation of all extensive consumers of fuel.

As regards petroleum for use in this country, the author is not sanguine. He thinks, and with good reason, that if a good supply of cheap mineral oils were available, its market price would quickly be raised above the point at which it could be advantageously used. Of course, the furnaces, &c., specially constructed for its consumption would become mere dead plant, a prospect which effectually deters industrialists from any attempts at its use.

Concerning gaseous fuels the author says little. We have in this country no extensive supply of natural gas. Coal gas, at any rate when furnished by companies, is too costly for use on the large scale, and "water-gas," except previously treated according to the Crookes patent, contains too much of the deadly constituent carbon monoxide to be consistent with safety. According to an analysis here given, it may contain 35·88 per cent.

Processes for desulphurising coal and coke are duly noted, including admixture with lime, chalk, soda, oxide of manganese, &c.; some of these processes were expected to yield at once a better coke and a purer gas. The author's opinion is that none of these methods have eliminated sufficient sulphur to justify their adoption on the large scale.

Among the more important additions made in the present edition, we notice methods for determining the ash of fuel. In coal and coke the ash is not merely a something to be subtracted from what would otherwise be the calorific value of the fuel, but it often interferes in a very annoying manner with the quality of the product to be obtained. Hence the metallurgist requires accurate and at the same time simple and expeditious methods for the analysis of his fuels. This want is well supplied in the work before us.

Chemists, engineers, &c., connected with metallurgical establishments or any works where fuel is extensively used, will find this manual of great service.

Gas Works; their Construction and Arrangement, and the Manufacture and Distillation of Coal Gas. Originally written by Samuel Hughes, C.E. Re-written and much Enlarged by William Richards, C.E. Eighth Edition, Revised, with notices of recent Improvements. London: Crosby Lockwood and Son.

When a technical work has reached its eighth edition the task of the reviewer is very much restricted. Still, we are compelled to point out one error, the more to be regretted on account of the wide circulation of the book. We refer to the favourable notice of Winsor or Windsor, whose real name was Winzer. This man gathered a knowledge of gas lighting from a memoir by Lebon, about ten years after the new illuminant had been practically introduced by Murdoch, came to England in 1802 or 1803, and described himself as the "discoverer, inventor, and patentee" of gas lighting. The fact is that he had contributed nothing whatever to the invention of gas, no more than to its manufacture. Our authors speak of his "extraordinary courage, perseverance, and zeal." These attributes, however, when employed in laying claim to the results of others generally receive less pleasant names. Possibly we may award to Winzer the somewhat questionable honour of having originated gas companies.

In Chapter III. we find carbon monoxide, or carbonic oxide, made to rank as a diluent of coal gas; but, on account of its fearfully poisonous nature we should place it upon the impurities. Our authors, though admitting its deadly character, do not consider it an impurity. It may be mentioned that the absence of sulphur compounds in coal gas is demanded more strictly in some Continental cities than in London.

On page 55 we are told that the hostile attitude of the coal interests to the public at large dates back to 1665, when the extortions of the dealers are characterised as having been excessive.

Attention is also drawn to the deterioration of coal by prolonged storage. We regret to find the word "caloric" occasionally used; we thought it had become obsolete even in its native country.

It appears that the iron oxide used for purification is often mixed with sawdust. This, we submit, must be disadvantageous if the spent mass is afterwards burnt in the kilns of sulphuric acid works, as it will be impossible to prevent the sulphurous acid given off from being more or less contaminated with carbonic acid.

Concerning test-papers, Twaddell hydrometers, alkalimeters, and test acid, we find the remarkable statement: "The only firm that supply them that we know of is A.

Wright and Co., Westminster." All these requisites can be obtained from any dealer in chemical apparatus.

The success of Cooper's patent for mixing lime with the coal before charging the retorts is here traced to the admission of a small quantity of air into the oxide purifiers. The advantages claimed by Cooper are admitted, but they are due to a different cause.

It is here said that the product saccharine was first obtained in the laboratory of the Beckton gas works.

The electric light is, of course, disparaged. Gas companies are told to seek improvements that the price of gas may be reduced, and to seek out new applications. This movement was already in progress, but the recent serious rise in the price of gas in which one at least of the London gas companies has indulged bids fair to put an end to gas cooking ranges. Many people who had introduced these useful appliances have found it necessary to lay them aside.

The work before us, though drawn up too much in the interest of gas companies, is undoubtedly ably written and useful.

The Construction of Gas Works Practically Described. By W. R. Herring, Manager Huddersfield Corporation Gas Department. With specially prepared Plates, Illustrations, and numerous useful Tables. London: Hazell, Watson, and Viney.

This work has evidently been drawn up with great care by an author who has no less evidently a thoroughly practical acquaintance with his subject. As an official of a municipal gas establishment, he does not adopt the "company" tone so unpleasant to all persons who are not shareholders. The substance of the work, however, lies for the most part outside our cognisance.

As regards the temperature to which the retorts are heated, the author says that the modern practice is to use high temperatures so as to produce a maximum yield per ton of coal. He states subsequently that at all temperatures above 980° much of the olefiant gas—the most luminiferous constituent—is eliminated; consequently the high heats now in vogue mean a sacrifice of quality to quantity.

It appears, especially in these days when strikes and rumours of strikes are rife, necessary for gas works to keep a considerable quantity of coal in store; but, as Mr. Herring points out, coal stored for whatever purpose rapidly deteriorates to the extent of 30 or 40 per cent in six months. Here is a powerful argument in favour of the proposal to generate gas close to the pit's mouth, using the coal as soon as brought up. In any case it would be well to adopt the author's simple suggestion of covering the coal stores at gas works with waterproof sheeting to exclude rain.

The coal "brasses" are a nuisance in the gas manufacture, as, indeed, in all the uses of coal, domestic or industrial. Mr. Herring proposes to give the men who "trim" the coal a premium over and above their wages on each cwt. of "brasses" picked out. This is well as far as lumps are concerned; but some coal contains iron sulphide disseminated through its entire mass in such fine specks and films that picking out is impossible. Hence the gas engineer, like the metallurgist, finds it necessary to keep a sharp watch on the quality of his coal.

As far as we are able to judge, this work may be highly recommended.

Manual of Assaying Gold, Silver, Copper, and Lead Ores. By Walter Lee Brown, B.Sc. Fourth Edition, 1892. Chicago: E. H. Sargent and Co.

Brown's "Manual of Assaying" has evidently given universal satisfaction both in America and Europe, or it would certainly not have reached its fourth edition in nine years This favourable opinion will, we think, be endorsed by all experts who have used it as a book of reference, and beginners will find it a safe guide.

The difficulty of defining assaying as distinct from analysis the author disposes of by confining the former term to dry methods, and the latter to those methods which chiefly employ liquid reagents. The electrolytic method (for copper at least) is made to rank as an analysis. Others, we must remember, adopt a different definition: they call a process analysis "when the end aimed at is the recognition and determination of all the constituents of an ore, an alloy, &c."; but assay when merely the percentage of some one valuable constituent is to be ascertained.

To one point in Mr. Brown's definition both of assaying and analysis we may take exception. He defines assaying as that branch of *exact science* which enables us, &c., whilst analysis effects the same results, &c. Now we submit that assaying and analysis alike are not branches of *science*, but industrial *arts*, based upon the sciences chemistry and physics.

The prices of some of the more important and costly articles of apparatus are given both in American and in English money. We do not know whether in calculating these prices due attention has been given to the circumstance that the price of any piece of apparatus made in Europe is enhanced in the United States by the peculiar fiscal system of the latter country. It is very questionable what claim the assays of copper, tin, cobalt, nickel, &c., have to be retained in presence of the improved and accelerated analytical methods. With gold and silver the case is different. The author fully admits that for copper the dry methods are inaccurate.

Mr. Brown by the production of this work has decidedly earned the gratitude of all persons interested in metallurgy and mining. The only alteration which we can suggest is that he should take a broader point of view, and in place of the principal minerals likely to contain gold, silver, copper, &c., found in the United States, he should give those of the known world.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l' Académie des Sciences. Vol. cxiv., No. 19, May 9, 1892.

Residual Life and the Functional Products of Tissues separated from the Living Being.—Arm. Gautier and L. Landi.—The authors show that vital processes still go on for a time in the tissues after the death of the entire animal.

On Sodium Trimethylcarbinol; Value of the Tertiary Alcohol Function.—M. de Forcrand.—A thermo-chemical paper not adapted for abstraction.

Action of Potassium Cyanide upon Ammoniacal Copper Chloride.—E. Fleurent.—The author has obtained long blue crystalline needles arranged in small tufts and of little stability, the ammonia rapidly escaping. Their composition is approximately—

$$2Cu_2Cy_2.CyNH_4.2NH_3.3H_2O.$$

The mother-liquor, after the escape of the ammonia, deposits fine green rectangular lamellæ, very stable, of the composition $2CuCy_2.Cu_2Cy_2.2NH_3.3H_2O$. These lamellæ are insoluble in water, but soluble in ammonia, from which they are deposited unchanged. They decompose at temperatures exceeding 100°. If treated with dilute acids they emit hydrocyanic acid and deposit cuprous cyanide. The solution from which these green crystals have been deposited, if set aside, yields lastly a mixture

of micaceous tablets and of other crystals which the author is examining.

Establishment of Fundamental Formulæ for the Calculation of the Moments of Maximum Inertia.—G. Hinrichs.—A purely mathematical paper.

Chemical Properties of Acetyl Fluoride and on its Analysis.—Maurice Meslans.—Water acts upon acetyl fluoride in an analogous manner to what it does upon acetyl chloride. Hydrofluoric and acetic acid are formed slowly and less energetically than in case of the chloride. If we treat the liquid acetyl fluoride with two or three volumes of cold water, the two liquids do not mix, but the fluoride disappears slowly. Potassa and soda in alkaline solutions quickly decompose acetyl fluoride, forming a mixture of alkaline fluoride and acetate. Quicklime introduced into a vessel filled with gaseous acetyl fluoride absorbs the gas, producing calcium fluoride and acetic anhydride. Gaseous ammonia reacts energetically upon liquid acetyl fluoride, producing a white crystalline mass, in which the microscope reveals the presence of two distinct substances. Aniline reacts powerfully upon acetyl fluoride, forming hydrofluoric acid and acetanilide melting at 115°. Absolute alcohol dissolves acetyl fluoride in every proportion, but the two substances do not react immediately. After prolonged contact in a closed vessel there are formed hydrofluoric acid and acetic ether, which may be separated on the addition of water. Amylic alcohol behaves in an analogous manner. Sodium amalgam and metallic sodium do not act sensibly upon liquid acetyl, but at dull redness sodium decomposes the gaseous fluoride with incandescence.

On Acid Pyrocatechine Antimonite.—H. Causse.—The compound in question is either a phenolic ether of antimonious acid or an acid pyrocatechine antimonite.

Action of Organic Acids upon the Acetylenic Carbides.—A. Béhal and A. Desgrez.—The acetylenic carbides, if strongly heated along with acetic acid, form instable compounds, which, in contact with water, are transformed into acetones. The reaction takes place in a sealed tube at 250°. The authors have operated upon œnanthylidene, caprylidene, butylmethylacetylene, and pentylmethylacetylene.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 74.

This issue does not contain any chemical matter.

Journal fur Praktische Chemie.
New Series, Vol. xlv., Part 1.

Our Knowledge of the Oximes and the So-called Stereo-Chemistry.—Ad. Claus.—A reply to a controversial paper by Auwers and Meyer, which appeared in the Berlin *Berichte*.

Communications from the Chemical Institute of the University of Kiel.—These consist of a paper by C. Stoehr on the pyridine and piperidine-bases of the β-series, in which the poisonous character of β-methylpiperidine and β-ethylpiperidine is experimentally shown. The phenomena produced resemble those occasioned by coniine.

On the So-called γ-Bromquinoline. — Hermann Decker.—Not adapted for useful abstraction.

The Addition of Sodium Acetacetic and Sodium Malonic Ethers to the Ethers of Unsaturated Acids.—A. Michael and O. Schulthess.—The authors communicate the results of their experiments on the addition of the former class of ethers to a series of ethers of the unsaturated polybasic fatty acids.

The Polymerisation of the Nitriles.—E. von Meyer.—The author controverts the views of Hanriot and Bouveault to be found in *Bull. Soc. Chimique*, li., p. 170.

Zeitschrift fur Anorganische Chemie.
Vol. i., Part 2.

On a Series of Trihaloid Compounds of Cæsium.—H. L. Wells.—With an "Account of their Crystallographic Properties," by S. L. Penfield.—This paper appears also in the *American Journal of Science*, 1892.

Contributions to Quantitative Spectroscopic Analysis.—G. Krüss and H. Krüss.—This valuable memoir will be reproduced as nearly as possible in full.

The Sulphocyanides of some Ammoniacal Compounds of Chromium.—Otto Nordenskiöld.—After some introductory matter with reference to the researches of Morland, Reinecke, and Cleve, the author examines the salts of chromodiaminsulphocyanide-hydrosulphocyanic acid and their derivatives, especially the ammonium salt, its reaction with aniline, its iodide, the potassium salt and its iodide, the barium, ferric mercury, silver, and aniline salts, chromodiamindianilidorthorhodanideaniline sulphocyanide, the piperidine salt, the free acid, and the mercuric sulphide compound of chromodiamintrisulphocyanide. In the second part Prof. Nordenskiöld examines the trisulphocyanides and their derivatives. Experiments to substitute N_2O with methyl sulphide were not successful. The author has also attempted to obtain a cobalt compound corresponding to these chromium compounds. Crystals were obtained which are not analogous to the chromium compounds. A brief notice is given of a paper by Odin T. Christensen on the "Compounds of Chromammonium Sulphocyanogen.

A New Direct Separation of Chlorine, Bromine, and Iodine.—P. Jannasch and K. Aschoff.—The authors have adopted the following method for the separation and gravimetric determination of the three halogens. The solution containing weighed quantities of sodium chloride, potassium bromide, and potassium iodide (about 0·3 grm.) of each salt was placed in a distillatory flask (which the authors figure) diluted with water to a volume of 750 c.c., and acidified by the addition of 5 c.c. of dilute sulphuric acid. The dilution is necessary to prevent the simultaneous escape of hydrochloric and hydrobromic acids. They then add to the cold liquid a solution of 1 grm. sodium nitrate in 10 c.c. water, when the flask must be instantly closed. The contents are at once turned to a reddish-brown colour by the liberation of iodine. The outlet tube of the flask is introduced into a cylinder, as deep as possible, of the capacity of 500 c.c., containing a mixture of 50 c.c. pure soda-lye, and 50 c.c. hydrogen peroxide, and is closed with a cork having two perforations. Through the second aperture of the cork passes a second glass tube bent twice at right angles and plunging with its longer limb into a flask containing the necessary quantity of the mixture of hydrogen peroxide and soda-lye, in order to keep back any traces of iodine which may be carried over mechanically. The cylinder is kept cold by being placed in cold water. A current of steam is then passed into the flask through the tube *a*, (the one which is *not* bent twice), the contents quickly become hot, and violet-coloured fumes of iodine fill the empty space, condensing in part in crystals in the cold portion of the outlet pipe, and being subsequently absorbed in the receiver. In about fourteen minutes the vessel becomes perfectly colourless, showing the complete expulsion of the iodine. The cylinder is then cautiously removed, and the immersed end of the tube is well rinsed with the washing-bottle. Not until then is the current of steam interrupted. The contents of the receivers are then entirely poured into a porcelain capsule which is covered, and heated on the water-bath after the further addition of 50 c.c. of the hydrogen peroxide solution for the complete oxidation of any traces of sodium nitrite. After the lapse of some hours solution of silver is added, whilst stirring, to the alkaline liquid. The brown precipitate first formed disappears on stirring, with formation of silver iodide, and the addition of silver nitrate is continued until the dark colour of the precipitate no

longer changes to yellow. The liquid is then acidified with nitric acid and heated for some hours on the water-bath until the silver iodide has been completely deposited, when it is filtered hot, dried, incinerated, fused, and weighed. The liquid should not be allowed to become cold. For the separation of the bromine and chlorine existing in the flask, the acid liquid is made distinctly alkaline with soda-lye. When it has been concentrated to about 50 c.c. it is returned to the flask, and when cold mixed with 60 c.c. dilute acetic acid (1 : 3 water), and with a concentrated solution of from 1 to 1·5 grm. permanganate. The two receivers are then connected with the flask, and a current of steam is introduced. An increasing turbidity of the liquid appears, and yellowish-red vapours of bromine are given off. The current of steam must not be too strong, the better to effect the complete absorption of the bromine by the soda-lye in the receiver. The distillation takes about forty-five minutes when the apparatus is disconnected; the contents of the receivers are poured into a porcelain capsule and heated for a time as above directed. Lastly, the precipitation of the bromine was effected with a mixture of silver solution and nitric acid (10 per cent silver solution and concentrated nitric acid). The silver bromide is filtered off and further treated as directed for iodine. The chlorine remains in the flask. For its determination the excess of permanganate is first reduced by adding soda-lye and alcohol and applying heat. The precipitate of manganese is filtered off and washed with luke-warm water. The clear filtrate is acidulated with nitric acid and the chlorine precipitated with silver nitrate.

Examination of the Atomic Weight of Copper.—Th. W. Richards.—The mean result of seven series of determinations is Cu = 63·605.

MISCELLANEOUS.

Has Sulphur been Decomposed ?—We mention, though not without strong doubts, the rumour that the elementary character of sulphur is in question. Dr. Gross is said to have been for many years engaged in exhaustive researches on this substance. He has communicated certain of his results at a meeting of the Physical Society of Berlin. Barium sulphide was fused in a silver crucible, and a powerful electric current was introduced by means of a platinum wire inserted in the melting mass. After some time it appeared that the barium had combined with the platinum to form a novel compound, whilst some 50 per cent of the sulphur had disappeared, leaving a corresponding quantity of a new substance in its place. Dr. Gross considers that sulphur is not an element, but the hydride of the new body. Several questions here suggest themselves, which it may be better to reserve, pending the appearance of further research on the question.

MEETINGS FOR THE WEEK.

TUESDAY, 31st.—Institute of Civil Engineers, 8. (Anniversary).
—— Royal Institution, 3. "Some Aspects of Greek Poetry," by Prof. R. C. Jebb.
—— Society of Arts, 8. "Lustre Ware," by William De Morgan.
THURSDAY, June 2nd.—Royal Institution, 3. "On Faust," by R. G. Moulton, M.A.
—— Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical, 8. "Ethylene Derivatives of Diazoamido Compounds," by R. Meldola, F.R.S., and F. W. Streatfeild, F.I.C.
FRIDAY, 3rd.—Royal Institution, 9. "Metallic Carbonyls," by Ludwig Mond, F.R.S.
—— Geologists' Association, 8.
—— Quekett Club, 8.
SATURDAY, 4th.—Royal Institution, 3. "Some Modern Discoveries in Agricultural and Forest Botany," by Prof. H. Marshall Ward, F.R.S.

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CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE

Edited by Wm. Crookes, F.R.S. (WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE") *Established Forty-Eight Years.*

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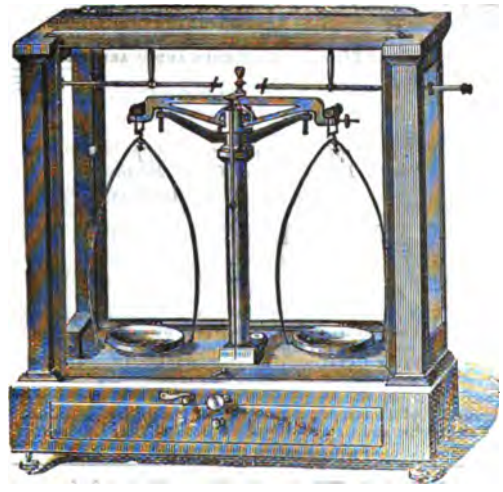

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THE CHEMICAL NEWS.

Vol. LXV., No. 1697.

NOTE ON THE SPONTANEOUS CONVERSION OF ISOPRENE INTO CAOUTCHOUC.*

By WILLIAM A. TILDEN, D.Sc., F.R.S.

Isoprene is a hydrocarbon which was discovered by Greville Williams many years ago among the products of the destructive distillation of indiarubber. Later, in 1884 (*Trans. Chem. Soc.*, xlv., 410), it was observed by myself among the more volatile compounds obtained by the action of a moderate heat upon oil of turpentine and other terpenes. It is a very volatile liquid, boiling at about 36°. Its molecular formula is C_5H_8, and it forms a tetrabromide, $C_5H_8Br_4$, but no metallic derivatives, like the true homologues of acetylene.

Bouchardat (*Comptes Rendus*, lxxxvii., 654, and lxxxix., 361 and 1117), observed that when isoprene is heated to a temperature near 300°, it gradually polymerises into a terpene which he called di-isoprene, but which is now usually called *dipentene*. This compound boils at 176°. A quantity of colophene similar to that which is produced by the action of heat upon turpentine is formed at the same time.

When isoprene is brought into contact with strong acids, aqueous hydrochloric acid for example, it is converted into a tough elastic solid, which has been examined by G. Bourchardat and by myself; it appears to be true indiarubber.

Specimens of isoprene were made from several terpenes in the course of my work on those compounds, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid the bottle contained a dense syrup, in which was floating several large masses of solid of a yellowish colour. Upon examination this turned out to be indiarubber. The change of isoprene by spontaneous polymerisation has not to my knowlege been observed before. I can only account for it by the hypothesis that a small quantity of acetic or formic acid had been produced by the oxidising action of the air, and that the presence of this compound had been the means of transforming the rest. The liquid was acid to test paper, and yielded a small portion of unchanged isoprene.

The artificial indiarubber, like natural rubber, appears to consist of two substances, one of which is more soluble in benzene or in carbon bisulphide than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characters with a similar preparation from Para rubber. The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound.

The constitutional formula of isoprene is not known with certainty, but it must be selected from the five following formulæ:—

$CH_3CH_2CH=C=CH_2$ $CH_3CH=C=CHCH_3$ $(CH_3)_2C=C=CH_2$	Derivatives of allene, $CH_2=C=CH_2$.
$CH_3CH=CH-CH=CH_2$ $CH_2=CCH_3-CH=CH_2$	Derived from crotonylene, $CH_2=CH-CH=CH_2$.

It is obvious that compounds such as these containing doubly-linked carbon may polymerise in a variety of ways, and in the present condition of our knowledge of the constitution, even of isoprene, it would be idle to speculate as to which out of the numerous possible arrangements would correspond to the constitution of caoutchouc.

* Paper read before the Philosophical Society of Birmingham, May 18, 1892.

ESTIMATION OF NITROGEN.

By VINCENT EDWARDS, F.C.S.

In a few remarks inserted in the Chemical News, lxv., p. 241, on the above subject, I fear I did not make myself sufficiently clear upon one point, which is, that when a sample is found by preliminary test to contain a fairly high amount of nitrate, the method will not succeed unless the usual modification (Scovell's) is carried out, or, in other words, the process will only answer with traces of nitrates along with ammoniacal and organic nitrogen.

I find that for the estimation of nitrogen in nitrates of soda and potash, the iron flasks are very convenient, economical and rapid, quite equalling in all but appearance the fancy sketches seen in some text-books. Care must be taken to try several blank determinations, as the iron filings give up some ammonia due to slow oxidation. Good quantities are 10 grms. of zinc grains, 5 grms. iron filings, ½ grm. of nitre, 100 c.c. of 30 per cent solution of potash, and 50 c.c. of water. This is allowed to stand for one hour, 100 c.c. more water added, and the ammonia distilled off into standard acid.

Lawes' Works, Barking,
May 31, 1892.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 261).

Description of Analyses.—First Series.

It is evident from the most probable constant error in Hampe's work lay in the great hygroscopic power of cupric sulphate dried at 250°. A possible means of detecting such error existed in the use of the crystallised salt as a starting point. This salt was therefore coarsely powdered, dried to constant weight over a mixture of crystallised and partially dehydrated cupric sulphate, and analysed by electrolysis in the usual fashion. Although the crystalline powder must have contained occluded water, the quantity of copper found in several samples from different sources was much larger than that demanded by the old atomic weight, and closely approached the theoretical quantity based upon the new value.

In the third experiment the weight of water lost by heating the salt to constant weight in the manner described by Hampe (*loc. cit.*) was also determined, and this amount proved to be nearly three-tenths of a per cent less than it should have been according to any hypothesis. Since larger crystals of cupric sulphate exposed to air above the desiccating mixture already mentioned lost none of their lustre, and since the salt under these conditions comes to perfectly constant weight, it seemed highly probable that the apparent deficiency of crystal water was due to occlusion in the so-called anhydrous salt, and not to any previous efflorescence of the crystals.

The sulphuric acid produced during the electrolysis†

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† In this connection it may be noted that Hart and Crossdale have quite independently used the sulphuric acid thus formed as a basis of alkalimetric analysis. (Chem. News, lxiii., 93, 1891). The idea appears to be a good one.

was preserved in each case, and approximately determined by means of the first preparation of sodic carbonate; also afterwards by the evaporation of the solution of sodic sulphate. Since the manipulation was more or less imperfect, and the materials and water not quite pure, it is thought unnecessary to include these somewhat bulky data in full here, but the evidence which they furnished was conclusive upon one point. The percentage of acid was not equal to the complement of the other percentages. In other words, over one-tenth of a per cent of material had not been determined.

Percentage of—	Found.	Theory Cu = 63·60.	Theory Cu = 63·33.
Water	35·958	36·0695	36·109
Copper	25·455	25·4665	25·385
SO_4	38·46±	38·464	38·506
Total.. ..	99·87	100·000	100·000

It is seen that we are dealing, not with infinitesimals, but with grave error, evident to the crudest analysis. The reason for the deficiency has already been suggested, but the proof is yet wanting.

The ratio between the copper and the sulphuric acid, or rather between the copper and sodic carbonate on the one hand, and sodic sulphate on the other, affords a new twofold basis for the calculation of the atomic weight of copper. This basis is entirely independent of the always uncertain weight of the cupric sulphate and the objectionable method of calculation from difference. The results correspond to the new atomic weight, but the complete discussion of this phase of the subject will be reserved until more definite data have been given. It is interesting to note that these comparatively crude experiments differ only by one or two units in the second decimal place of the result from the far more carefully executed work yet to be described.

Analysis of Cupric Sulphate.—First Series: Data and Results.

(Weights reduced to vacuum standard).

No. of Expt.	Weight cupric sulphate (cryst.).	Weight $CuSO_4$ (250°) found.	Weight copper found.	Per cent water lost at 250°.	Per cent copper.
1.	2·8815	—	0·7337	—	25·462
2.	2·7152	—	0·6911	—	25·452
3.	3·4639	2·2184	0·8817	35·958	25·454
		Average		35·958	25·455

Second Series.

Although from the earlier experiments it appeared that the deficiency in the sum of the analytical results might be explained by the hypothesis of the existence of water in the so-called anhydrous cupric sulphate, it was possible that at least a part of this deficiency might be due to experimental error. The next step of the research was therefore to start again upon a more refined basis. It was important, too, that some proof of the above mentioned hypothesis more definite than an indirect inference should be obtained. The clearest idea of the various operations may probably be acquired through a detailed statement of one of the experiments, and accordingly such a statement is given below.

Experiment 4.—The cupric sulphate (see p. 245), having been cautiously powdered in an agate mortar and dried to constant weight over the desiccating mixture already described, was gradually heated to 255° in a platinum crucible with a very closely fitting lid.

The crucible and contents gained in weight upon the balance pan at a rate of only one-tenth of a milligrm. in four minutes, and hence the last weighing is without doubt sufficiently accurate. When the weight had thus become constant, 20 drops of strong pure sulphuric acid were added to the white powder, and the whole was kept

	Grms.
Weight of crucible + $CuSO_4.5H_2O$	=23·36188
„ „ alone	=20·30300
„ cupric sulphate in air	= 3·05888
Correction to vacuum (sp. gr. =2·274)..	= 0·00118
Corrected weight $CuSO_4.5H_2O$, in vacuum..	= 3·06006
Weight crucible + $CuSO_4$ dried for three hours at 255°	=22·26243
Weight crucible dried for two hours more..	=22·26233

at a temperature of 365° for three and one-half hours in a suitable air bath composed of a nest of porcelain crucibles. An air thermometer was used in measuring the temperature.

	Grms.
Weight of crucible and contents	=22·25905
The same, after re-heating for four hours with six drops more of H_2SO_4	=22·25900
Weight in air of cupric sulphate dried at 365°	= 1·95600
Weight in vacuum of cupric sulphate (sp. gr.*=3·61)	= 1·95637
Loss of weight between 255° and 365°.. ..	= 0·00333

The crucible and contents gained in weight even less rapidly than before.

This experiment shows that the so-called anhydrous cupric sulphate of Hampe *loses about seventeen one-hundredths of a per cent of its weight* when subjected to the temperature of the boiling point of mercury; a loss nearly equal to the deficiency which we are seeking to explain. The residual salt may be slowly dissolved in water without the need of very great caution. It gives a perfectly clear solution, which is neutral to methyl orange and does not deposit basic salt even upon indefinite standing. These facts alone show that the decrease in weight was not due to loss of acid, but a much more definite proof of this point is given later.

For electrolysis, the clear solution of the 1·95637 grms. of cupric sulphate was transferred to a large platinum crucible. This crucible had been previously coated inside with pure copper, washed with water and alcohol, and dried at 103°. The crucible was supported upon a platinum triangle in the interior of a large beaker, and was covered by a watch glass into which was fused the positive electrode. The wires conducting the current into the beaker were of platinum. The whole apparatus was covered with a large watch glass, which effectually excluded impurity. Several times before the conclusion of the electrolysis the drops adhering to the inner watch glass were washed back into the crucible by means of apparatus especially adapted for the purpose. After the maintenance for one hundred and twenty hours of a weak current (*Proc. Amer. Acad. Arts Sci.*, xxv., 202), the electrolysis was interrupted, and every trace of the acid in the crucible was washed as rapidly as was consistent with scrupulous care into a large platinum bottle. The crucible was then washed with pure alcohol, dried at 103°, and finally weighed.

	Grms.
Crucible+Cu before electrolysis (Bar. =767; $t°$= 20°)	=36·12120
Crucible + additional Cu after (Bar. = 750; $t°$ = 20°)	=36·90000
Apparent weight of copper	= 0·77880
Correction for change in temperature and pressure	=+0·00007
Correction to vacuum	=−0·00001
True weight of copper in vacuum..	= 0·77886

* This is a mean of the results of Hampe and Karsten.

	Per cent.
Percentage of copper in $CuSO_4.5H_2O$.. ..	= 25·452
,, ,, $CuSO_4$ dried at 255°	= 39·744
,, ,, ,, ,, 250° (Hampe)..	= 39·725
Percentage of copper in $CuSO_4$ dried at 365°	= 39·811

Further comment here is unnecessary.

The earlier experiments had already shown approximately the equivalent ratio of sodic carbonate to copper. Accordingly a very little less than the amount of sodic carbonate corresponding to the data above was carefully weighed out from the second sample of this material, and the salt was ignited at a dull red heat until constant in weight. (See description of sodic carbonate, p. 260).

	Grms.
Weight crucible + Na_2CO_3	=21·60095
,, ,, alone	=20·30260
,, sodic carbonate in air	= 1·29835
Weight sodic carbonate in vacuum (sp. gr. =2·466)	= 1·29880

The sodic carbonate was dissolved in water and poured into the very dilute solution of sulphuric acid which had been formed by the electrolysis. The lid of the crucible, as well as that vessel itself, was very thoroughly washed with water. On account of the great dilution of the liquid, carbonic anhydride was not at once set free, but upon warming for six or eight hours upon the steam-bath it was easily expelled. During this operation the platinum flask was of course suitably covered, a Gooch crucible being found most convenient for this purpose.

When gas evolution had long ceased, the solution was wholly transferred to a large platinum dish, and was evaporated on the steam-bath to a volume of about 50 c.c. The very slight excess of acid was then titrated by means of sodic hydroxide, using methyl orange as an indicator, and was found to require 0·09 c.c. of a decinormal solution for neutralisation. The probable error of the end point was not greater than one drop, or one ten-thousandth part of the sodic carbonate present.

	Grms.
Sodic carbonate weighed out	=1·2988
,, ,, added in titration	=0·0005
,, ,, required (in vacuum)	=1·2993
Cupric sulphate taken ($CuSO_4.5H_2O$)	=3·06006
Copper found in ,, ...	=0·77886

Per cent of SO_4 in $CuSO_4.5H_2O$ = 38·439

Atomic weight of copper:

$Na_2CO_3 : Cu = 106·108 : 63·606$

In transferring the sodic sulphate from the evaporating dish to the capacious platinum crucible in which it was to be weighed, the precaution of washing with water which had been thoroughly boiled was absolutely essential to prevent the possibility of subsequent mechanical loss during evaporation. At best, the concentration of a solution in an open crucible over the steam-bath is an unsatisfactory operation, and accordingly for the third series a new method was devised. The water left the sodic sulphate very slowly; but in the end it evaporated so completely that after covering there was a scarcely audible decrepitation on heating the crucible to redness. The pure white sodic sulphate was finally fused at a bright red heat. During this last operation the salt occasionally became tinged with a slightly yellowish hue, due probably to a trace of iron from the platinum vessels; but the purest specimens remained wholly colourless. The salt lost only one or two-tenths of a m.grm. during the fusion. A drop of very dilute permanganate solution was not decolourised by the solution of the residual salt, showing that no reduction had taken place. A very small amount of insoluble residue, consisting of the apparently unavoidable impurity in the sodic carbonate together with any iron or copper which might be present, was determined in each case; and the amount was subtracted from the weight of sodic sulphate. Naturally, besides this, it is necessary to subtract the amount of salt corresponding to the *acid* added in titrating back and forth when determining the end point of the acidimetric reaction. This end point had been taken as the average of a number of readings. Below are the data of the experiment under discussion.

	Grms.
Weight of crucible + Na_2SO_4 (&c.)	= 18·67040
,, ,, alone	= 16·92594
Uncorrected weight of Na_2SO_4..	= 1·74446
Subtract weight of salt added in titration .	= 0·00362
,, ,, insoluble residue.. ..	= 0·00034
Corrected weight of Na_2SO_4 in air	= 1·74050
Correction to vacuum (Sp. gr. = 2·631)..	= +0·00063
Weight Na_2SO_4 in vacuum	= 1·74113

Per cent of SO_4 in $CuSO_4.5H_2O$ = 38·445

,, ,, ,, ,, found above = 38·439

Atomic weight of copper (if Na_2SO_4 = 142·166, from table):

Weight Na_2SO_4 : weight Cu = 142·166 : 63·595.

No copper was found in the solution of the sodic sulphate, and a minute trace only in the insoluble residue.

The object of the second experiment of the series was

Analysis of Cupric Sulphate.—Second Series: Data.

(Weights reduced to vacuum standard).

No. of Experiment.	$CuSO_4.5H_2O$ taken. Grms.	$CuSO_4$ (260°) taken. Grms.	$CuSO_4$ (360°) found. Grms.	Metallic copper found. Grms.	Sodic carbonate required. Methyl orange. Grms.	Sodic carbonate required. Phenolphthalein. Grms.	Sodic sulphate found. Grms.
4	3·06006	1·9597	1·95637	0·77886	1·2993	—	1·7411
5	2·81840	1·8048	—	0·71740	—	—	—
6	7·50490	4·8064	4·79826	1·90973	3·1859	3·1865	4·2679

Second Series.—Results.

No. of Experiment.	Water lost at 260°.	Additional loss at 360°.	Total per cent of water (360°).	Per cent of copper.	Per cent of SO_4 by Na_2CO_3 (average).	Per cent of SO_4 by Na_2SO_4.
4	35·959	0·109	36·068	25·452	38·439	38·444
5	35·964	—	—	25·454	—	—
6	35·957	0·108	36·065	25·446	38·435	38·424
Averages ..	35·960	0·108	36·067	25·450	38·437	38·434

to determine whether the method of weighing cupric sulphate in a tightly covered crucible was an accurate one. The determination was in every respect modelled after the mode of procedure adopted by Hampe, a tightly-stoppered weighing-bottle being used to contain the salt. The result sufficiently confirmed the previous experiment. For later experiments a crucible was accordingly used, since the evaporation of sulphuric acid at high temperatures is much more feasible in such an apparatus. A mishap prevented the accurate determination of the acid.

For the third experiment a much larger amount of material was used, the method being essentially that of the first experiment. The large crucible of 150 c.c. capacity used for the electrolysis was not previously coated with copper. The end point of the acidimetric determination was taken with both phenolphthalein and methyl orange, the colour change with the latter indicator being rather unsatisfactory in the presence of so large an amount of dissolved substance. The amount of insoluble residue found in the sodic sulphate was only 0·0003 grm.; it contained no trace of copper. The results showed that little was to be gained by the use of larger quantities of substance, since the unavoidable errors of quantitative work were multiplied nearly in proportion to the quantities of material. Mechanical errors are at the present day inessential compared with the constant ones which complicate so many analyses. It is obvious that a far more accurate result could be obtained from four-tenths of a grm. of really anhydrous cupric sulphate than from 400 grms. of a substance still retaining nearly two-tenths of a per cent of water.

Adding in the small amount of water which is lost by cupric sulphate between 255° and 365°, the percentage composition of the crystallised salt, as indicated by the second series of analyses, gives a much more satisfactory total result than before:—

Water lost at 255°	=35·960
Additional water lost at 365° ..	= 0·108
Copper	=25·450
Sulphuric acid radicle	=38·436
Total ..	=99·954

Although greatly improved, the analysis still leaves much to be desired. Even in materials prepared with the described precautions, traces of impurity were manifest. In the last experiment, where a large amount of material was used, a few minute spots, which might have been arsenic, appeared on the clear surface of the electrolytic copper, and traces of a brownish colouration were observed upon the positive pole. Both of these impurities were so infinitesimal in amount that they could not reasonably have been expected seriously to affect the final result; but the thought that they might be responsible for a part of the remaining deficiency prompted the execution of a still more elaborate series of experiments. The data and results of the second series are appended.

(To be continued).

METHODS OF ANALYSIS OF DAIRY PRODUCTS.

Official Methods of Analysis of the Association of Official Agricultural Chemists for 1890-91.

Butter.

Microscopic Examination.

Place a small portion of the fresh sample taken from the inside of the mass on a slide, add a drop of pure sweet oil, cover with gentle pressure, and examine with a one-half to one-eighth inch objective for crystals of lard, &c.

Examine same specimen with polarised light and selenite plate without the use of oil.

Pure fresh butter will neither show crystals nor a parti-coloured field with selenite. Other fats melted and cooled, and mixed with butter will usually present crystals and variegated colours with the selenite plate.

For further microscopic study dissolve 4 or 5 c.c. of the fat in 15 c.c. of ether in a test tube. Stopper the tube with cotton-wool loosely, and allow to stand twelve to twenty-four hours at room temperature (20°—25°). When crystals form at the bottom of the tube, they are removed with a pipette or glass rod or tube, placed on a slide, covered, and examined. The crystals formed by later deposits may be examined in a similar way.

Sampling.—If large quantities of butter are to be sampled, a butter trier or sampler may be used. The portions thus drawn, about 500 grms., are to be perfectly melted in a closed vessel at as low a heat as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous. A portion is then poured into a vessel from which it is to be weighed out for analysis, and should nearly or quite fill it. This sample should be kept in a cold place till analysed.

Determination of Water.—1·5 to 2·5 grms. are dried to constant weight at the temperature of boiling water in a dish with flat bottom, having a surface of at least 20 c.m.^{2}.

The use of clean dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom is employed.

Determination of Fat.—The dry butter from the water determination is dissolved in the dish with *absolute* ether or with 76° benzene. The contents of the dish are then transferred to a weighed Gooch filter with the aid of a wash bottle filled with the solvent, and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of fat is calculated from the data obtained.

Substitute Method for Fat.—Water may be determined by drying the butter on asbestos or sand, and the fat extracted by *anhydrous alcohol-free* ether in an extraction apparatus. The extract, after evaporation of the ether, is heated to constant weight at the temperature of boiling water and weighed.

Determination of Casein and Ash.—The crucible containing the residue from the fat determination, consisting of casein and ash, is covered and heated gently at first, gradually raising the temperature to just below red heat. The cover may then be removed and the heat continued till the contents of the crucible are white. The loss in weight of the crucible and contents represents casein, and the residue in the crucible, mineral matter. In this mineral matter, dissolved in water slightly acidulated, chlorine may be determined gravimetrically with silver nitrate, or volumetrically, using potassium chromate as indicator.

Estimation of Salt (NaCl).

Volumetric Method.—The amount of the butter or butter substitute to be taken is from 5—10 grms.; weigh in a counterpoised beaker glass. The butter (fresh from the refrigerator) is placed in portions of about 1 grm. at a time in the beaker, these portions being taken from different parts of the sample. By this means a reasonably fair sample of the whole is obtained.

The given quantity having been weighed out, it is removed from the pan.

Hot water is now added (about 20 c.c.) to the beaker containing the butter, and after it has melted the liquid is poured into the bulb of the separating apparatus. The stopper is now inserted, and the contents shaken for a few moments.

After standing until the fat has all collected on top of the water, the stop-cock is opened, and the water, containing most of the salt, is allowed to run into an Erlenmeyer flask, being careful to let none of the fat globules pass.

Hot water is again added to the beaker, and thence

poured into the separatory apparatus, the bottle well shaken, and the foregoing process is repeated from ten to fifteen times, using each time 10 to 20 c.c. of water.

The resulting washings contain all but a mere trace of the NaCl originally present in the butter.

Estimation of NaCl in Filtrate.—The chloride of sodium is now determined in the filtrate by a standard solution of $AgNO_3$, using a few drops of a saturated solution of potassium chromate as indicator.

Specific Gravity.

Weight of Flask.—Use a small specific gravity flask of from 25 to 30 c.c. capacity. The stopper should be bevelled to a fine edge on top, and the lower end should be slightly concave to avoid any trapping of air. The flask is to be thoroughly washed with hot water, alcohol, and ether, and then dried from thirty minutes to one hour at 100°. After cooling in a desiccator the weight of the flask and stopper is accurately determined.

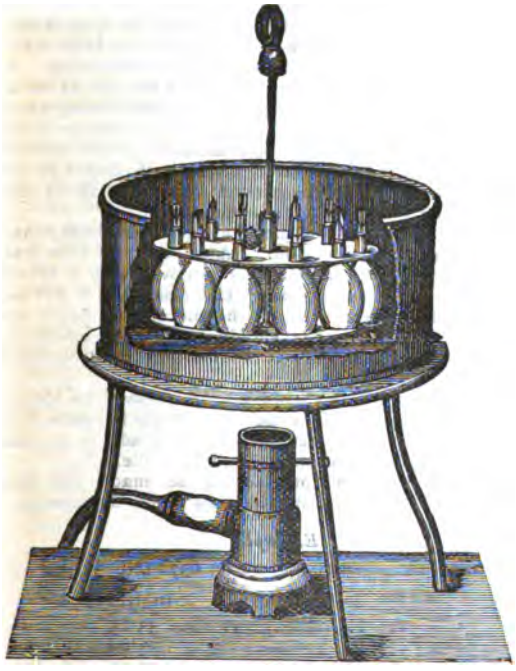

Fig. 1.

Weight of Water.—The flask in an appropriate holder (Fig. 1), conveniently made of galvanised iron, is filled with freshly boiled and still hot distilled water, and placed in a bath of pure, very hot, distilled water in such a way that it is entirely surrounded by the liquid with the exception of the top.

The water of the bath is kept in brisk ebullition for thirty minutes, any evaporation from the flask being replaced by the addition of boiling distilled water. The stopper* is then inserted, the flask removed, wiped dry, and after it is nearly cooled to room temperature, placed in the balance and weighed when balance temperature is reached. A convenient size of holder will enable the analyst to use eight flasks at once. The temperature at which water boils in each locality may also be determined; but unless at very high altitudes, or on days of unusual barometric disturbance, the variations will not be great, and will not appreciably affect the results.

* The stopper should be kept for a few minutes before use in hot distilled water.

Alternate Method of Estimating the Weight of Water in Flasks.

Computation by the Formula of Landolt.

Formula for calculating volume V, in c.c., of a glass vessel from the weight P of water of temperature t contained therein, and the volume V′ at any other temperature t' (from Landolt and Börnstein's "Physical-Chemical Tables," p. 39, Table 17):—

$$V = P\,\frac{p}{d}$$

$$V' = P\,\frac{p}{d}\,[1+\gamma\,(t'-t)]$$

p = weight (in brass weights) of 1 c.c. H_2O in vacuo; see formula Table 3. (This is so nearly 1 that it will not

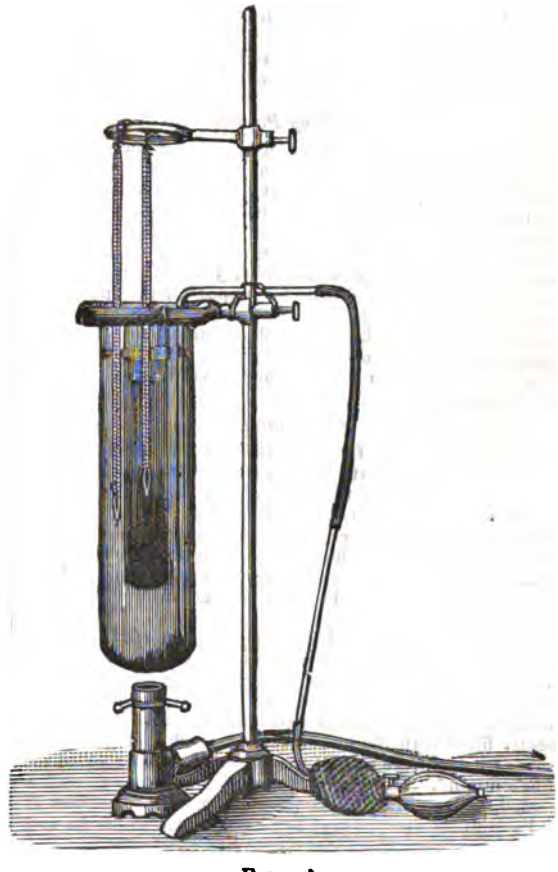

Fig. 2.

affect the result in the fifth place of decimals, and may therefore be disregarded). Hence the formula stands:—

$$V' = P\,\frac{1}{d}\,[1+\gamma\,(t'-t)]$$

d = density of water at temperature t (see Table 12).

γ = 0·000025, the cubical expansion coefficient of glass.

From this volume the weight of the water may be readily obtained by referring to Tables 13 and 13*a*.

Weight of Fat at Water-Boiling Temperature.—The flask is emptied of its water, rinsed with alcohol and ether, and dried again for a few minutes at 100°. It is then filled with the dry, hot, fresh-filtered fat, which should be entirely free from air bubbles.

The stoppered flask is then replaced in the water-bath,

kept for thirty minutes at the temperature of boiling water, removed, and treated as above. The weight of fat having been determined, the specific gravity is obtained by dividing it by the weight of water previously found.

Example.

	Grms.
Weight of flask No. 22, dry	10·0197
„ „ „ plus water	37·3412
„ water	27·3215
„ flask No. 22, plus fat	34·6111
„ fat	24·5914

Specific gravity = 24·5914 ÷ 27·3215 = 0·90008.

The weight of the flask dry and empty, and the weight of water at 99° to 100° contained therein, may be used constantly if great care be taken in handling and cleaning the apparatus.

Example.

	Grms.
Weight of flask No. 10, dry and empty ..	10·0028
„ „ after three weeks' use ..	10·0030

Melting-Point.

The apparatus for determining the melting-point (shown in Fig. 2) consists of (1) an accurate thermometer for reading easily tenths of a degree; (2) a cathetometer for reading the thermometer (this may be done with an eye-glass if held steadily and properly adjusted); (3) a thermometer; (4) a tall beaker glass, 35 c.m. high and 10 c.m. in diameter; (5) a test-tube, 30 c.m. long and 3·5 c.m. in diameter; (6) a stand for supporting the apparatus; (7) some method of stirring the water in the beaker, for example, a blowing bulb of rubber, and a bent glass tube extending to near the bottom of the beaker; (8) a mixture of alcohol and water of the same specific gravity as the fat to be examined.

Manipulation.

The disks of the fat are prepared as follows:—The melted and filtered fat is allowed to fall from a dropping tube from a height of 15 to 20 c.m. on to a smooth piece of ice floating in water. The disks thus formed are from 1 to 1·5 c.m. in diameter, and weigh about 200 m.grms. By pressing the ice under the water the disks are made to float on the surface, whence they are easily removed with a steel spatula, which should be cooled in the ice water before using.

The mixture of alcohol and water is prepared by boiling distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot, the water is poured into the test-tube already described until it is nearly half full. The test-tube is then nearly filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled, the mixture will contain so many air bubbles as to be unfit for use. These bubbles will gather on the disk of fat as the temperature rises, and finally force it to the top of the mixture.

The test-tube containing the alcohol and water is placed in a tall beaker containing water and ice. The disk of fat is dropped into the tube from the spatula, and at once sinks until it reaches a part of the tube where the density of the alcohol water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

The delicate thermometer is placed in the test-tube and lowered until the bulb is just above the disk. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disk, the thermometer is moved from time to time in a circularly pendulous manner. A tube prepared in this way will be suitable for use for several days; in fact, until the air bubbles begin to attach themselves to the disk of fat. In no case did the two liquids become so thoroughly mixed as to lose the property of holding the disk at a fixed point, even when they were kept for several weeks.

In practice, owing to the absorption of air, it has been found necessary to prepare new solutions every third or fourth day.

The disk having been placed in position, the water in the beaker glass is slowly heated and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol water mixture rises to about 6° below the melting-point, the disk of fat begins to shrivel, and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle is even with the centre of the bulb. The bulb of the thermometer should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotary movement should be given to the thermometer bulb, which might be done with a kind of clockwork. The rise of temperature should be so regulated that the last 2° of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so, the reading of the thermometer is to be made. As soon as the temperature is taken, the test-tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. The test tube (ice water being used as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum about 1·5° above the melting-point of the fat under examination.

Working thus with two tubes, about three determinations can be made in an hour. After the test-tube has been cooled the globule of fat is removed with a small cup attached to a wire before another disk of fat is put in.

The distilled water in which the piece of ice floats, on which the disks are made, should be recently boiled to free it of all air particles. It is important that the disks be free from air bubbles.

The edge of the disk should not be allowed to touch the sides of the tube. This accident rarely happens, but in case it should take place and the disk adhere to the sides of the tube, a new trial should be made.

Triplicate determinations should be made, and the second and third results should show a near agreement.

Example.

Melting-point of sample of butter 6372 (No. 3):—

	Degrees C.
1	33·15
2	33·05
3	33·00

(To be continued.)

CONTRIBUTIONS TO QUANTITATIVE SPECTRAL ANALYSIS.

By G. KRÜSS and H. KRÜSS.

THE methods of spectrophotometry or quantitative spectral analysis have of late years been increasingly used both in analysis and in the decision of theoretical questions. Quantitative spectral analysis presents a wide field both in organic and inorganic chemistry, and we hope that the following communications may be of some use in analytical practice:—

1. *Comparison of the Various Methods of Spectroscopic Quantitative Analysis.*

One of the chief conditions for obtaining good results in such determinations is working with a spectrum a

pure as possible—that is, with the smallest practicable widths of slit. The diminution of the width of the slit, however, has its limits, since the edges of the slit, however carefully ground, are never mathematical right lines. Still, with well-made apparatus, the width of the slit may be reduced to 0·003 or 0·004 m.m. without the observation being disturbed by the appearance of transverse bands in the spectrum. In opposition to the advantage due to the purity of the spectrum comes the limitation of light owing to the reduced width of the slit. In quantitative spectroscopic work we have to arrange that as much as possible of the light falling upon the slit may reach the eye of the observer, and that a relative maximum of light reaches the slit. The latter point may be attained on whatever principle we are working. A comparison between the two methods, that of Vierordt with a symmetrical double slit and that of the polarisation spectro-photometric procedure, shows that Vierordt's method enables us more perfectly to work with a pure spectrum.

The authors show that all the polarisation spectrophotometers have a feebler luminosity, and therefore, the quantities of incident light being equal, require a greater width of slit than Vierordt's double-slit spectro-photometer.

This defect may be remedied by illuminating the slit, if practicable, by means of an electric light.—*Zeitschrift fur Angew. Chemie.*

A METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. BROWNING.

At the suggestions of Prof. F. A. Gooch, and following the general mode of procedure laid down in his paper (*Am. Chem. Jour.*, ix., p. 33) upon the separation of sodium and potassium from lithium by the action of amyl alcohol on the chlorides, I undertook a series of experiments looking toward the separation of strontium from calcium by the action of amyl alcohol on the nitrates. On boiling several portions of the so-called chemically pure calcium and strontium nitrates with amyl alcohol, nearly complete solubility was observed in case of the calcium salt, while corresponding insolubility seemed to be characteristic of the strontium salt, and these results seemed to warrant proceeding with the work.

For the quantitative tests to be described, standard solutions of specially purified strontium and calcium nitrates were prepared. In general the preparation was effected by precipitating a soluble salt of either element with ammonium carbonate in the presence of ammonium chloride, washing thoroughly with boiling water, dissolving in the least possible amount of nitric acid, and making up to measure. In the earlier experiments other methods of purification were used, such as the precipitation of the strontium nitrate by alcohol, and in case of the calcium salt the preparation of the nitrate from the carbonate precipitated by ammonium carbonate from a solution of calcium sulphate. The method first described, however, gave satisfactory results, the spectroscope failing to show in the product thus obtained any trace of intermixture of calcium and strontium salts, or the presence of any other appreciable impurity. In the determination of the standards of these solutions definite amounts were drawn off from burettes into counterpoised beakers or crucibles (according as the method of determination was by precipitation or evaporation) and weighed as a check on the burette reading. The strontium nitrate in each portion was converted into the sulphate, either by precipitation in the presence of alcohol, or by evaporating and igniting, these methods yielding results closely agreeing. The calcium was determined by evaporation with sulphuric acid. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon strontium nitrate alone. Accordingly several amounts of the strontium salt were measured from a burette into counterpoised Bohemian beakers of about 100 c.m.³ capacity and weighed. The water was then evaporated over a water bath, and the dry salts dissolved in a few drops of water and boiled with 30 c.m.³ of amyl alcohol, that amount being determined upon for convenience. Care should be taken not to add more than the necessary amount of water to dissolve the salt, inasmuch as the presence of much water delays the process (it being necessary to expel all the water before the amyl alcohol can do its work) and tends to cause spattering due to the superheating of the water and consequent sudden generation of steam under the alcohol. It has been my experience that in the presence of a few drops of water the boiling goes on quietly, the water escaping easily through the amyl alcohol, so that in the course of a few minutes the alcohol reaches its normal boiling temperature (128—130° C.). In order that the inflammable fumes of the alcohol might not reach the flame during the boiling, the beaker was placed upon a piece of asbestos board about 15 c.m. square. When the temperature of the alcohol reached its normal boiling point (128—130° C.), as shown by a thermometer, the beaker was removed and the strontium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed.

The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of strontium nitrate were removed from the beaker by washing with small amounts of previously boiled amyl alcohol contained in a wash bottle, the mouthpiece of which consisted of a small chloride of calcium tube passing through the stopper and drawn out and plugged at the lower end with cotton to exclude particles of the calcium salt from the alcohol. By this device the introduction of moisture into the amyl alcohol was guarded against. The crucible containing the strontium nitrate was placed in an air bath and heated to 150° C. to drive off all amyl alcohol, and weighed. A constant weight was obtained uniformly in one treatment. Series I. contains the results of these experiments, the strontium being calculated as oxide.

Series I.

	SrO taken. Grm.	SrO found. Grm.	Loss. Grm.
1.	0·1229	0·1220	0·0009
2.	0·1231	0·1221	0·0010
3.	0·1230	0·1219	0·0011
4.	0·1227	0·1213	0·0014

These results suggested a possible solubility of the strontium salt, and accordingly experiments were made to test this point. Amounts of strontium nitrate closely agreeing with those above were taken and treated in the same manner. The filtrates amounting, without the washings, to about 25 c.m.³ were evaporated to dryness. The residue was ignited to burn off organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness, and weighed. In two cases the residue of strontium sulphate was found to contain of the oxide respectively 0·0009 grm. and 0·0010 grm. As will be seen, the solubility of the strontium nitrate averages about 0·0010 grm. of the oxide to 30 c.m.³ of amyl alcohol used. The exact extent of this solubility depends, of course, upon the amount of amyl alcohol remaining after boiling; and, since the source of heat is removed as soon as the normal boiling temperature of the alcohol is reached, very little decrease in the volume of the previously boiled alcohol results. On measuring the amounts

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xliii., January, 1892

of the alcohol remaining in several experiments I found them to approximate closely to 25 c.m.³. It seemed justifiable, therefore, to add as a correction to the apparent amount of strontium oxide found 0·0010 grm. for every 25 c.m.³ of amyl alcohol remaining, or for every 30 c.m.³ originally taken. Experiments were also made to determine whether the strontium nitrate might have been at all broken down in the process of boiling and heating, so that some strontium might be present in the final residue in the form of oxide or nitrite. In two of these experiments portions of strontium nitrate left by the treatment with amyl alcohol were dissolved, precipitated as the sulphate and weighed as such, and the results of these experiments (5 and 6) go to show that the composition of the strontium nitrate is not appreciably changed in the process of separation and drying. In certain other experiments directed to the same end, the residues of the process of separation were, after weighing and drying, treated with a drop of nitric acid, and again dried at 150° C. and weighed. These tests (7 and 8) confirm the indications of the previous experiments. Finally, a third experiment was made upon strontium nitrate dried at 150° C. to see what decomposition might result by heating to temperatures somewhat higher than 150° C.,—the temperature at which the residues of the previous experiments had been dried. The result shows that the loss in the twenty-five degrees above 150° C. is exceedingly slight.

		Grm.
(5)	$Sr(NO_3)_2$ calculated as SrO	0·1219
	The same dissolved and precipitated as $SrSO_4$ calculated as SrO	0·1219
(6)	$Sr(NO_3)_2$ calculated as SrO..	0·1213
	The same dissolved and precipitated as $SrSO_4$ calculated as SrO	0·1214
(7)	$Sr(NO_3)_2$ calculated as SrO..	0·1228
	The same dried at 150° C. after adding a drop of HNO_3	0·1228
(8)	$Sr(NO_3)_2$ calculated as SrO..	0·1239
	The same dried at 150° C. after adding a drop of HNO_3	0·1239
(9)	Weight of $Sr(NO_3)_2$ dried at 150° C.	0·2482
	Weight of the same portion dried at 165° C.	0·2480
	Weight of the same portion dried at 175° C.	0·2478

When calcium nitrate was treated in a similar manner by boiling with amyl alchol the mass of the salt dissolved, but minute portions separated out on the bottom or sides of the beaker. Such residues were, however, very small, and on weighing were found not to exceed 0·0003 grm. or 0·0004 grm. of the oxide. In several instances this insoluble residue was washed thoroughly with ethyl alcohol, dissolved in water, tested before the spectroscope and found to give the characteristic calcium spectrum. All experience pointed to the fact that the formations of the residue was due to some very slight change of composition of the calcium nitrate. On one or two occasions the acidified solution of the residue appear to reduce a drop of an extremely dilute solution of potassium permanganate, and this action suggested the presence of a nitrite. Treatment of this residue with nitric acid and subsequent evaporation of the excess of acid failed, however, to leave the calcium salt in a condition to be dissolved by amyl alcohol.

It is possible, therefore, that the real cause of insolubility is to be sought in the oxidation of the amyl alcohol and consequent formation of an organic acid, and, subsequently, of the corresponding calcium salt, but the amounts of the residue were so extremely small that it was not practicable to solve this question at once exactly and satisfactorily without directing attention too far from the main issue. Moreover, the error introduced by this peculiar behaviour of the calcium salt proved to be insignificant in its effects upon the quantitative determination of the calcium, and accordingly it was disregarded in the subsequent tests.

(To be continued.)

NOTICES OF BOOKS.

Watts's Dictionary of Chemistry. Revised and entirely Re-written. By H. Forster Morley, M.A., D.Sc., and M. M. Pattison Muir, M.A. Assisted by Eminent Contributors. In 4 volumes, Vol. III. London and New York: Longmans, Green, and Co., 1892. Large 8vo., pp. 856.

This volume extends from indigocarboxylic acid to phenyltetrazolecarboxylic acid, and comprises a number of exceedingly important articles, nearly all characterised by fulness of detail, clear arrangement, sound general views, and remarkable brevity of expression. Particular attention is due to the memoir on the "Periodic Law" by Douglas Carnegie. The writer notices the memoir produced in 1862 by Béguyer de Chancourtois, which, though published in the *Comptes Rendus*, strangely failed to attract public attention even in France until disinterred by Lecoq de Boisbaudran. The claims of Newlands are admitted, but with the reservation, that his law "was retrospective rather than phophetic." It is also conceded that the periodic law was nothing else than a generalised and developed form of the law of octaves, the conceptions underlying both laws being practically identical." The respective contributions of L. Meyer, of Hartley, Carnelley, Prudhomme, Watts, Roberts-Austen, and others to the theory are duly appreciated. Mendeleeff's views on the nature and origin of the elements are briefly noticed. It may here suffice to say that the great Russian chemist is not favourable to the idea of the origin of the elements by a process of evolution.

Prof. H. E. Armstrong, F.R.S., contributes an article on isomerism, in which the varied and fluctuating connotations of the terms isomerism, polymerism, metamerism, is pointed out. Especial reference is made to the use of these terms by Wanklyn, Kekulé, Tilden, McGowan, and others. Attention is here given to the arrangement of atoms in space according to the hypothesis of Van 't Hoff and Le Bel.

Isomorphism is discussed at considerable length and with great ability by Dr. Hutchinson. The relations known as polymorphism, morphotrophy, isomorphotropy, and isogonism are successively expounded.

Ozone is ably discussed by Mr. Shenstone, of Clifton College. In these days, when it has been proposed to re-name this substance "electric gas," it may be useful to remind the world that ozone may be produced without the aid of electricity. It may also grieve some persons to learn that, according to Schöne, the presence of ozone in the atmosphere is still not proven. Antozone, which at one time attracted no little attention, is now considered to be simply hydrogen peroxide.

A suggestive and elaborate paper is that on the rare metals from the pen of W. Crookes, F.R.S. The author shows the complexity not merely of the crude minerals from which the so-called rare earths have been obtained, but in many cases even of the earths themselves. He suggests that these earths when they have been split up as far as possible, may be found to contain nearly sixty unknown bodies. Before any such substance can be recognised as elementary it must, Mr. Crookes suggests, be submitted to a more severe scrutiny than any body of this class has yet undergone. Pending the completion of this scrutiny he recommends that they should be designated as "quasi- or meta-elements,"—aggregates intermediate in rank between the molecules with which we have to deal in chemical reactions and the ultimate atoms.

Here the reader may compare the section on the molecular constitution of bodies supplied by Prof. J. G. Thomson, F.R.S.

The great difficulty to be encountered by the editors of, and to a less degree by the contributors to, such works as the present, consists in the continued stream of discoveries which supplement and sometimes modify or even

cancel a part of our former knowledge. The work when complete will be simply invaluable.

A Practical Introduction to Chemistry: being the *Practical* Introductory Course of Work in Use at Clifton College. By W. A. Shenstone, Lecturer on Chemistry in Clifton College. With Illustrations. New and Revised Edition (Third Edition). London and New York: Longmans, Green, and Co., 1892.

Concerning this book, there has occurred a slight irregularity which has for the moment puzzled us, and has, we fear, occasioned annoyance to the author.

A few weeks ago we received from the publishers a copy as of a "new edition," but bearing the date 1887. This was reviewed in our issue of May 13. Now, however, the real "new and revised edition" of the present year has reached us—the "third edition" as it is called in the introduction. This we have now accordingly the pleasure of examining. We find that it extends to 120 pages in place of 101 pages, as in the former edition. It opens with instructions on cutting and bending glass, a subject on which Mr. Shenstone can speak with recognised authority. It then treats of the balance and its use. The former edition commenced with the lessons to be learnt from the phenomena of burning, and gave less complete information on glass-working and the balance in the form of appendices.

The section on "burning" has been improved. The experiment showing that air will burn in an atmosphere of coal gas is calculated to prove very instructive. In fact, most of the operations recommended are well planned to cause the pupil to observe and to understand what he observes. The illustrations will be found neater and clearer than those in the former edition or editions.

The entire work, it will be found, contains no reference to examinations, and no advice to pupils supposed to be preparing for such deceptive ordeals. Nor did we in our brief and, under the peculiar circumstances, somewhat perfunctory notice of the second edition assert or even insinuate to the contrary. We merely raised the general question whether our exceptional number of elementary manuals stands in any causal connection with our national system of education. On the very contrary, we think that Mr. Shenstone's pupils are to be congratulated on the rational character of their course of training, and we wish his work could be substituted for some dozen others which we have had the pain of reading through.

Les Matierès Grasses, Caracterès, Falsifications, et Essai des Huiles, Beurres, Graisses, Suifs, et Cires. ("Fatty Matters: Characters, Falsifications and Assay of Oils, Butters, Fats, Tallows, and Waxes.") By Dr. Georges Beauvissage. Paris: Librairie J. B. Baillière et Fils, 1891. 16mo., pp. 324.

This volume pertains to a series now being issued by the publishers under the title "Bibliothèque des Connaissances Utiles," and treats of a most important class of substances,—a class interesting both on account of their many applications in the arts and of the varied and ingenious frauds of which they are the subject.

The author begins by drawing a distinction between fatty matters and fats. The latter are definite proximate principles of a known and fixed composition, ethers of glyceryl. The fatty matters, on the contrary, are variable mixtures of such principles. As the physical characters of the fats he mentions their condition as liquid or solid, their melting and congealing-points, which, curiously enough, are not in all cases absolutely identical, a phenomenon due in part to their feeble conductivity for heat, their specific gravity, and their solubility. Secondary physical properties which, however, have often to be taken into consideration in determining the nature of a specimen, are their fluidity, their refractive action, their coefficient of expansion, and their electric conductivity.

The methods of ascertaining these properties are fully and carefully described. In taking the specific gravity of an oil he recommends Regnault's bottle, and the areothermic balance of Dalican and Eudeville. This apparatus, as here figured, seems to be exactly identical with the Mohr-Westphal balance, so well-known in the laboratory.

The cohesion-figures of Chatin and the diazometer of Rousseau are also described. For determining the relative fluidity of oils the author recommends Barbey's exometre. For ascertaining the refractive action of oils the author mentions the Abbe refractometer and the oleorefractometer of Amagat and Ferdinand Jean, which requires for comparison a standard oil prepared by F. Jean, the refraction of which is null. Jean has also devised a special instrument for applying the Maumené test, the difference of temperature of an oil before and after treatment with sulphuric acid.

The examination of cod-liver oil takes a prominent place. We regret to find that the author seems to prefer the brown oils, the colour of which is due simply to the incipient decomposition of the nitrogenous tissues. It is doubtless true that pale oils artificially bleached have lost their medicinal value, but this is no argument against the natural pale oils obtained from livers which have had no time to putrefy. The detection of the sophistications of oils is rendered extremely difficult by the rarity of absolutely genuine specimens for comparison.

Butters, fats, and tallows, form the subject of Part III. In deciding upon the character of a butter great weight is laid upon its refractive power. Abbe's refractometer is regarded as inapplicable on account of the difficulty of keeping the sample melted at a constant temperature, whilst the apparatus of Amagat and F. Jean is of easy use. By means of this instrument the deviation of pure butter of the best quality is +35°, that of oleomargarine only +5°, that of cotton-oil +20°. Lard, suets, &c., give − deviations. Thus the detection of these frauds is comparatively easy.

The colouration of butters with annatto must be pronounced a disgusting fraud, in view of the fact that this dye-ware is often worked up with stale urine, and has been found swarming with microbia.

Of all the fatty matters added to or used as substitutes for cow-butter the most to be approved is cocoanut butter, which in taste is scarcely distinguishable from the product of the cow, and is certain to be free from morbific micro-organisms. Tallows, it is shown, may contain some of the earlier stages of the dreaded tape-worm, *i.e.*, the cisticerci.

The fourth part of the book treats of waxes, animal, vegetable, and mineral.

This book, small as is its compass, is extremely rich in useful matter. Not merely the most trustworthy analytical processes, but the properties of the oils and fats, are clearly and accurately described. It must be strongly recommended both to analysts and to chemical industrialists.

Explosives Act, 1875 (38 Vict., c. 17).—*Sixteenth Annual Report of Hér Majesty's Inspectors of Explosives, being their Annual Report for the Year* 1891. London: Hér Majesty's Stationery Office. Also Eyre and Spottiswoode, Fleet Street and Abingdon Street; J. Menzies and Co., Edinburgh and Glasgow; and Hodges, Figgis, and Co., Dublin.

This report may be considered satisfactory. The law concerning the manufacture and storage of explosives, if not perfect, certainly does not err in the direction of needless stringency, and the inspectors are evidently discharging their duties with great care and discretion. Fault can be found only with the local authorities, who are sometimes apt to impose penalties disproportionately small.

Only one death has occurred during the year from

accidents by fire or explosion during the process of manufacture. The total number of factories under continuing certificate and licence is 125, in addition to 123 so-called "toy firework" factories.

Twelve new explosives have been added to the authorised list; these, however, present no decidedly novel features. A great variety of smokeless or quasi-smokeless powders are now on the market.

Proceedings for irregularities in factories are now rare. In one case only was it necessary to put the law in force. The illegal manufacture of fireworks still occurs; one offender in Lambeth was only detected in consequence of an accident, and was fined £25 and costs.

The precautions necessary for the electric lighting of factories for explosives have required considerable attention. Illegal storage has rendered proceedings necessary in nine cases. A firm at Chesterfield were fined £4 for keeping detonators in an unauthorised place, so that they were stolen by a boy and distributed among his companions. The importance of keeping explosives out of the way of children and youths has been fully shown by the accidents which have happened in the course of the year. Not a few mishaps are due to the absurd custom of allowing miners, &c., to store in their houses the powder required in their daily work.

Many of the accidents occurring during the use and conveyance of explosives are due to conduct which was not merely grossly illegal, but, even more, decidedly irrational. Careless thawing of dynamite, blasting gelatin, &c., has given rise to no little mischief. In consequence, Nobel's Explosives Company have deemed it necessary to send round a special warning to their customers.

The number of outrages with explosives in Great Britain and Ireland, although not so great as in certain foreign parts, is enough to occasion a painful sense of uneasiness and justify the question whether the convenience of "high" explosives in engineering and military operations really compensates for the facilities they afford to the criminal classes.

The account of the tremendous explosion which took place at Rome on April 23, 1891, presents some very instructive features. The seismometers at the Alban Hills Observatory, at the distance of eighteen miles, showed three distinct earth waves, thus proving, as in the great Stowmarket case of 1871, that in severe explosions the shock is conveyed not merely in the air, but also through the ground. The explosion was ascribed to the spontaneous ignition of parachute or signal rockets. The committee of investigation denounced "mixed storage," which in this country is never sanctioned.

A very interesting explosion took place at the Schlebusch Dynamite Factory, near Cologne, on June 3. The magazine contained 1200 kilos. of nitroglycerin, was exploded by lightning in spite of the conductors which had been examined in May, and had been found in perfect order.

Some drunken men at Cheyenne placed a target against a magazine containing 1200 lbs. gunpowder, 600 lbs. dynamite, and a quantity of detonators. After a few shots they succeeded in blowing up the magazine and themselves.

Two samples of gun-cotton were examined which may lay claim to a historical character. One of these was taken in 1887 from the river passing the gun-cotton works at Stowmarket, having thus been under water since August 11, 1871. The other was dug up in February, 1891, on the site of the old exploded magazine of the same factory, and had been buried for 19½ years. Both samples were in perfect condition without any sign of deterioration. This not only proves the stability of well-made gun-cotton, but shows the good quality of the gun-cotton exploded on the memorable 11th of August, and that, as the chemists who gave evidence at the inquest unanimously concluded, the mischief was occasioned by a portion of the gun-cotton having been maliciously tampered with.

The use of the electric light in magazines or factories does not necessarily exclude all danger. If a glow-lamp is broken in an atmosphere of gunpowder dust the carbon filament may for a moment retain heat enough to ignite the suspended dust. This was experimentally demonstrated at the Waltham Abbey Gunpowder Factory. There are the further risks from short-circuiting, heating of conductors, and sparking. The possible fall of a lamp from any cause must also be considered.

It is to be hoped that the action of the inspectors will gradually educate the public up to a higher grade of intelligence concerning the possession and the use of explosives. Even coroners, magistrates, &c., are at present sometimes in a perilous state of ignorance.

Elements of Physics. By C. E. Fessenden, Principal of the Collegiate Institute, Peterborough, Ontario. London and New York: Macmillan and Co., 1892, pp. 229.

This little work is by no means devoid of commendable features. The introductory chapter on matter and its properties is admirably written. We do not assert that the views advanced are novel, but they are put in a manner which must be fully intelligible to the young. We cannot help admiring the manner in which the attention of the pupil is called to facts which are always at hand, and from which the elementary truths of physics may be gathered. Thus he is quietly trained in the great arts of observing phenomena, and deriving from them the right conclusions,—the double process,—of which at the very least three-fourths of the business of our life consists. The term "phenomenon" is well explained, but explained as ably as it may be, the quacks have once for all got hold of it and will persist in its misuse as long as the English language is spoken.

As regards the scale of hardness of minerals the author has committed an error, clerical or typographical, in ascribing it to Mohr in place of Mohs. A careful student will be able to learn from this book not merely the elements of physics, but what is of even wider importance, the art of observation.

The Late Professor A. W. von Hofmann.—The interment of this illustrious *savant* took place on the 9th ult. Baron von Mirbach, on behalf of the Emperor and Empress, placed a splendid wreath upon the coffin. The Empress Frederick, the Grand Duchess of Baden, and the town of Giessen had also sent magnificent floral offerings. The Minister of Public Instruction was unable to be personally present, but was represented by Dr. Althoff. The University was represented by the Rector, Dr. Foerster, the Judge of the University Court, Daude, and the Dean, Prof. Diels. The Academy of Sciences was represented by the perpetual secretaries, Professors Auwers and Mommsen, the Imperial Physico-technical Institute by Privy Councillor von Helmholtz, the Patent Office by Privy Councillor Rommel, and the Imperial Sanitary Office by Dr. Koehler. The Technical High School and the Agricultural High School were represented by their Rectors. Numerous Universities and Chemical Societies had sent splendid garlands. The most distinguished representatives of the various Societies took part in the ceremonies. The eulogium was pronounced by P. Stechow. The students of the first chemical institute of the University opened the procession to the cemetery. Then followed the funeral car drawn by six horses, and the carriages with the mourners; whilst the great body of the students with numerous banners closed the procession.—*Chemiker Zeitung.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 20, May 16, 1892.

Contribution to the History of the Silico-carbon Compounds.—P. Schützenberger.—Some years ago, the author, in conjunction with M. Colson, described certain tertiary compounds consisting of carbon, silicon, and oxygen, or of carbon, silicon, and nitrogen. They are obtained by heating crystalline silicon to a red-white heat either in an atmosphere of carbonic acid or of carburetted gas and nitrogen. All these compounds are powders of a green colour, infusible, not attacked by hydrofluoric acid and by caustic alkalies even in concentrated solutions. They are attacked at nascent redness by melting potassa. In all, the carbon associated with silicon resists combustion at a red heat by means of free oxygen or of copper oxide. The carbon of these compounds can be burnt only on heating these compounds to redness along with basic lead chromate. The author has since obtained a new silicon carbide, SiC. This compound is a light green powder not attacked by boiling solution of potassa or by hydrofluoric acid, infusible and fixed.

Method for Separating the Xylenes.—J. M. Crafts.—For separating the xylenes, a weighed quantity of 10 to 20 grms. of the crude sample is added to 2½ parts of concentrated sulphuric acid in a tube of Bohemian glass. The length in millimetres occupied by the stratum of xylene is measured, and the tube is sealed and heated for an hour to 120°, shaking it vigorously. A saturated hydrocarbon remains on the surface as an insoluble stratum, but before measuring it is necessary to add 3 or 4 parts of a mixture of equal volumes of hydrochloric acid and of water, shaking, and allowing it to settle for an hour, so as to separate a portion which has been dissolved by the sulphonic acid. The tube must not be allowed to cool entirely to avoid a deposition of crystals. The hydrocarbon is measured and separated by means of a parting funnel; the acid solution is returned to the tube, which is sealed again and heated to 122° for twenty hours. By this treatment 97 per cent of the metaxylene are separated in a layer which is measured. The measurement is controlled by weighing after the metaxylene has been distilled with water to eliminate certain black substances; an operation which involves a loss of about 0·2 grm. The sulphones of the para- and ortho-xylenes and of ethylbenzene show only mere traces of decomposition at 122°. If heated more strongly they are decomposed without distinct fractionation, and it is advantageous to recover the whole by heating the solution after the removal of the metaxylene to 175° for twenty hours. The three recovered hydrocarbons are dissolved in three portions of sulphuric acid, and a volume of concentrated hydrochloric acid is added to the solution when cold. When the metaxylene has been separated, the sulphone of the paraxylene alone is precipitated in fine slender lamellæ, which are washed in concentrated hydrochloric acid upon an asbestos filter until the washings no longer give a reaction with barium chloride. The crystals are then exposed to the air until their weight is constant in order to find the proportion of paraxylene. The orthoxylene and ethylbenzene are finally separated by the process given by M. Friedel and the author in the "Dictionnaire de Wurtz" (Supplement, p. 1655).

Mechanical Determination of the Boiling Points of Compounds, with a Simple Terminal Substitution.—G. Hinrichs.—This paper is not adapted for useful abstraction.

Proximate Analysis of Chlorophyllic Extracts. Nature of Chlorophyllone.—A. Etard.—The author's procedure may be summarised as follows:—The green plants, dried at the ordinary temperature and coarsely powdered, are completely exhausted in the cold by means of carbon disulphide acting upon at least 4 kilos. of the dried material. After distilling off the solvent there remains an extract of a waxy consistence. Alcoholic extracts, if prepared directly, are so complex that their analysis may be regarded as impossible. *Sulphocarbonic Extracts. Group* 1.—The solid waxy extract if ground up with cold alcohol until this solvent runs off colourless, leaves a greenish mass, which on successive crystallisations, first from benzene, and then from acetic ether in presence of animal charcoal, always yields substances perfectly white and often well crystallised. These substances are solid carbides and high alcohols, glycols, and glycerines. *Group* 2.—The alcoholic mother-liquors are distilled *in vacuo*, the residue taken up in potassa at 2 per cent, and an excess of ether, contains alkaloids, alcohols, glycols, and chlorophylls. *Group* 3.—The preceding alkaline solution if acidulated in presence of ether yield to the latter saturated fatty acids. *Alcoholic Extracts. Group* 4.—The alcoholic extract (from material previously exhausted with carbon disulphide) prepared in heat and then solidified by concentration, is exhausted by grinding up with cold alcohol in presence of its own volume at least of ground glass. There remains a solid residue which is titrated with ether. Group 4, which the ether leaves as a residue, contains extractive matters free from chlorophyll, of an astringent taste, and generally of a brown colour. *Group* 5.—The ethereal extract from the foregoing process yields on evaporation chlorophylls capable of separation and purification. *Group* 6.—The alcoholic solutions from Group 4 distilled *in vacuo* leave a residue from which cold ether extracts a large quantity of very green chlorophyll. *Group* 7.—The residue insoluble in ether derived from the foregoing group contains extractive matters nearly colourless, soluble in water and alcohol, and mostly nitrogenous. The hypochlorine of Pringsheim is probably, according to Tchirsch, identical with the chlorophyllane of Hoppe-Seyler. It is very doubtful whether it is a definite chemical individual.

Influence of the Nature of the Soil upon Vegetation.—J. Raulin.—In experiments with potatoes the author found the crop decrease in proportion as the clay and limestone in the soil were augmented, but increased with increasing proportions of sand and humus.

Zeitschrift fur Anorganische Chemie. Vol. i., Part 3.

Research on the Atomic Weight of Copper.—Th. Richards.—Second communication. In part already inserted. (See Chemical News, vol. lxv., p. 236).

New Method for the Titration of Ferric Salts.—Hermann Moraht.—The volumetric method here proposed depends on the two best known reactions of ferric oxide, *i.e.*, on the formation of prussian blue from a ferric salt and potassium ferrocyanide, and the production of red iron sulphocyanide by means of potassium sulphocyanide. The solution of a ferric salt gives with ferrocyanide a precipitate of prussian blue, until all the ferric oxide present has been thrown down. Even a solution of iron sulphocyanide is precipitated and decolourised by potassium ferrocyanide. If a solution which, in addition to suspended prussian blue, still contains traces of a ferric salt, is mixed with potassium sulphocyanide as an indicator, the red colour of iron sulphocyanide appears. But on the further addition of potassium ferrocyanide this colour must disappear with a furthur formation of prussian blue at the moment when all the existing iron has been transformed into this compound. It was above all things necessary to assume that prussian blue is a chemical individual of the constant composition $Fe_4(FeCy_6)_3$, as it has been proved by A. Classen (Mohr's "Titriermethode," sixth edition, 1886, p. 235). A second necessity is to render the end of the precipitation and the disappearance

of the red colour distinctly visible. This is easily effected, as prussian blue is quite insoluble in ether, which readily dissolves iron sulphocyanide. The latter compound can be withdrawn from very dilute aqueous solutions by shaking out with ether. In carrying out the titration of ferric salts on the above principle the reaction between the ferric salt and the ferrocyanide must be effected in bottles with well-fitting ground stoppers, shaking violently. The opening of the bottles must be performed very cautiously so as to minimise the evaporation of ether. In order to obtain very exact results it is recommended to effect two titrations, the first as a preliminary and the second as final. The ferric solution in question, or an aliquot portion, is mixed in a ½-litre stoppered bottle with a little potassium sulphocyanide and about 50 c.c. of ether, so as to take at once a deep red colour. Solution of potassium ferrocyanide of known strength is then gradually added from a burette, shaking the bottle violently each time until after settling the supernatant stratum of ether appears of a faint rose or colourless. After this preliminary experiment the ferric solution, or an aliquot portion of it, is put in a ½-litre stoppered bottle, mixed with nearly the number of c.c. of ferrocyanide solution which were used in the preliminary experiment, stirred up, and the potassium sulphocyanide and a sufficient quantity of ether are then added. After shaking and allowing the two liquids to separate, the ether appears only of a very faint rose-colour, and one or a few drops of the ferrocyanide suffice to decolourise it completely. The colourless character of the supernatant ether may best be recognised on viewing it obliquely from below. The standard of the ferrocyanide may be found by dissolving weighed quantities of pure iron in hydrochloric acid with the addition of a little potassium chlorate, expelling *all* the excess of chlorine by ebullition and determining the number of c.c. of the solution of ferrocyanide which are necessary to convert the ferric salt present into prussian blue. We thus obtain directly the quantity of iron corresponding to 1 c.c. of the standard solution. No ferrous salt must be present along with the ferric compound.

Contributions to a Knowledge of the Compounds of Palladium. — Michael Frankel. — This important memoir will, if possible, be inserted in full.

Possibility of a Gaseous State of Certain Metals at Temperatures below their Melting-Point.—W. Spring.—We notice the following experiment:—Leaflets of silver, platinum, and gold, were heated to 150° with concentrated hydrochloric acid in sealed tubes. The metals were dissolved and the chlorides formed were reduced by the hydrogen evolved from the metals and the hydrochloric acid. They were deposited on the sides of the tubes in microscopic crystals. It may be assumed that in this experiment even the platinum existed for some time as a liquid before taking a crystalline form.

The Direct Quantitative Separation of Chlorine, Bromine, and Iodine.—P. Jannasch and K. Aschoff.—Certain inaccuracies which the authors encountered in their earliest experiments are traced to the use of an impure acetic acid.

Quantitative Separation of Iodine and Chlorine by direct Precipitation with Solution of Thallium Sulphate.—P. Jannasch and K. Aschoff.—Hübner, Spezia, and Frerichs have some time ago made known a method for the determination (partly gravimetric and partly volumetric), of iodine in presence of chlorine or bromine, depending on the sparing solubility and the yellow colour of thallous iodide. The method proposed by the authors for separating I and Cl by means of thallium sulphate is purely gravimetric, and depends on the absolute insolubility of thallous iodide in cold water containing alcohol even in presence of ammonium salts and other compounds in which thallium chloride remains in solution. A separation of bromine and chlorine in the above manner seems not possible, since thallous bromide is in all cases too soluble.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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MEETINGS FOR THE WEEK.

TUESDAY, 7th—Photographic, 8.
—— Royal Institution, 3. "Some Aspects of Greek Poetry," by Prof. R. C. Jebb.
WEDNESDAY, 8th.—Geological, 8.
THURSDAY, 9th.—Royal Institution, 3. "On Faust," by R. G. Moulton, M.A.
—— Mathematical, 8.
FRIDAY, 10th.—Royal Institution, 9. "Magnetic Properties of Liquid Oxygen," by Prof. Dewar, F.R.S.
—— Astronomical, 8.
—— Physical, 5. "Some Points connected with the Electromotive Force of Secondary Batteries," by Dr. J. H. Gladstone and Mr. Hibbert. "Workshop, Ballistic, and other Shielded Galvanometers," by Prof. W. E. Ayrton and Mr. Mather.
SATURDAY, 11th.—Royal Institution, 3. "Some Modern Discoveries in Agricultural and Forest Botany," by Prof. H. Marshall Ward, F.R.S.

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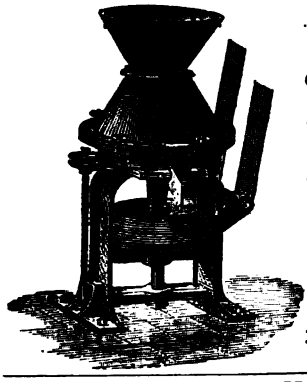

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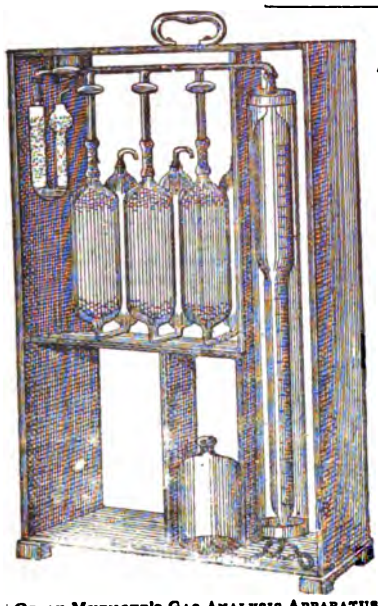

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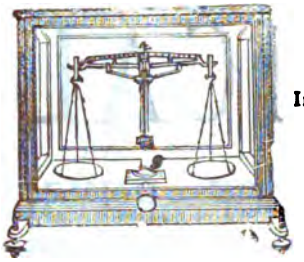

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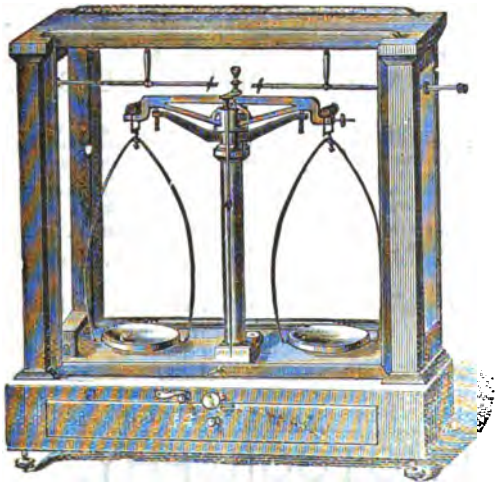

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THE CHEMICAL NEWS.

VOL. LXV., No. 1698.

RESOLUTIONS ADOPTED BY THE INTERNATIONAL COMMISSION FOR THE REFORM OF CHEMICAL NOMENCLATURE ASSEMBLED AT GENEVA FROM THE 19TH TO THE 22ND APRIL, 1892.

1. THAT in addition to the usual name, each organic compound shall have an official name assigned to it, enabling it to be found under a distinct heading in tables and dictionaries. The Commission expresses the wish that authors would adopt the habit of mentioning in their memoirs the official name in parenthesis along with the name which they have selected.

2. That for the present only the nomenclature of compounds of known constitution be considered, the question of bodies of unknown constitution being postponed.

I.—*Hydrocarbons.*

3. The termination *ane* is to be adopted for all the saturated hydrocarbons.

4. The present names of the four first normal saturated hydrocarbons (*methane*, *ethane*, *propane*, *butane*) are to be retained; names taken from Greek numerals to be used for those which contain more than four atoms of carbon.

5. Hydrocarbons with arborescent chains are to be regarded as derivatives of the normal hydrocarbons, and their name is referred to the longest normal chain which can be established in their formula, adding the designation of the lateral chains.

$CH_3(CH_3)CH-CH_3$ Methylpropane.

6. When a hydrocarbon radicle is introduced into a lateral chain, metho-, etho-, &c., is to be used in place of methyl-, ethyl-, &c., prefixes reserved for cases where substitution takes place in the principal chain.

$CH_3-CH_2-CH_2-CH(CH_3)(CH_3)-CH_2-CH_2-CH_3$ Metho-ethyl-heptane.

7. The position of the lateral chains is to be indicated by figures indicating to which of the carbon atoms of the principal chain they are attached. The numbering is to commence from that end of the principal which is nearest to a lateral chain. In case the two lateral chains nearest to the extremities are placed symmetrically the preference is to be given to the simplest.

(1) (2) (3) (4) (5) (6)
$CH_3-CH(CH_3)(CH_3)-CH_2-CH_2-CH_3$. Methyl-3-hexane.

(1) (2) (3) (4) (5) (6)
$CH_3-CH(CH_3)(CH_3)-CH(CH_2-CH_3)(CH_2-CH_3)$. Methyl-3-ethyl-4-hexane.

8. The atoms of carbon of a lateral chain are to be designated by the same figure as the atom of carbon to which the chain is attached, with the addition of an index fixing their rank in the lateral chain, setting out from the point of attachment.

(1) (2) (3) (4) (5) (6) (7)
$CH_3(CH_3)(2^1)-CH-CH_2-CH(4^1\ CH_2-4^2\ CH_3)-CH_2-CH_2-6H_3$.

9. In case of two lateral chains attached to the same atom of carbon, the order in which these chains are announced is to correspond to their order of complication, and the simplest indices are to be accented.

10. The same method of numbering is to be adopted for lateral chains connected to closed chains.

11. In non-saturated hydrocarbons with an open chain possessing a single double connection, for the termination *ane* of the corresponding saturated hydrocarbon the termination *ene* is to be substituted; if there are two double connections the name is to end in *diene*, if three in *triene*, &c.

$CH_2=CH_2$. Ethene.
$CH_2=C=CH_2$ Propadiene.

12. In like manner the names of hydrocarbons with triple connection are to terminate in *ine*, *di-ine*, *tri-ine*.

$CH\equiv CH_2$. Ethine.
$CH\equiv C-CH_2-CH_2-C\equiv CH$. Hexadiine.

13. If there are simultaneously double and triple connections, the terminations *enine*, *dienine*, &c., are to be used.

14. The non-saturated hydrocarbons are to be numbered like the corresponding saturated hydrocarbons. In case of ambiguity or of the absence of a lateral chain, the number 1 is to be attached to the terminal carbon nearest the connection of the highest order.

(1) (2) (3) (4) (5)
$CH_3(CH_3)CH-CH_2-CH=CH_2$.

(1) (2) (3) (4) (5)
$CH\equiv C-CH_2-CH_4=CH_2$.

15. If necessary, the place of the double or triple connection is to be indicated by the number of the first carbon atom to which it is attached.

$CH_2=CH-CH_2-CH_3$. Butene 1.
$CH_3-CH=CH-CH_3$. ,, 2.

16. The saturated hydrocarbons with closed chains are to take the names of the corresponding saturated hydrocarbons of the fatty series, preceded by the prefix *cyclo* (cyclohexane for hexamethylene).

17. The numbering of the hydrocarbons is to be preserved in all their substitution products.

II.—*Functions.*

18. *Alcohols* and the *phenols* are to be designated by the name of the hydrocarbon from which they are derived, followed by the suffix *ol* (methanol, pentenol).

19. In the case of polyhydric alcohols or phenols, between the name of the fundamental hydrocarbon and the suffix one of the particles *di*, *tri*, *tetra*, indicating hydricity, is to be interposed (propanetriol for glycerin, hexanehexol for mannite).

20. The name mercaptan is abandoned, and this function is to be expressed by the suffix *thiol* (ethane-thiol).

21. The oxy ethers are to be designated by the names of the component hydrocarbons, connected by the particle *oxy* (a provisional decision).

$C_5H_{11}-O-C_2H_5$. Pentane-oxy-ethane.
$C_6H_5-O-CH_3$. Benzene-oxy-methane.

22. The sulphides are to be designated by the syllable *thio*, the disulphides by *dithio*, the sulphones by *sulphone* (a provisional decision).

$C_6H_5-S-C_2H_5$. Benzene-thio-ethane.
$C_6H_5-S-S-C_6H_5$. Benzene-dithio-benzene.
$C_6H_5-SO_2-C_6H_5$. Benzene-sulphone-benzene.

23. The *aldehydes* are to be characterised by the suffix *al* added to the name of the hydrocarbon whence they are derived, and the sulphuretted aldehydes by the suffix *thial*.

HCOH. Methanal.
CH_3-CSH. Ethane thial.

24. The *ketones* are to receive the termination *one*.

$CH_3—CO—CH_3$. Propanone.
$CH_3—CO—CH_2—CH_3—CH_3$. Pentanone 2.

The diketones, triketones, thioketones, are to be desig nated by the suffixes *dione*, *trione*, *thione*.

25. The present nomenclature of the *quinones* is to be retained.

26. The name of the monobasic acids of the fatty series is to be taken from that of the corresponding hydrocarbon followed by the suffix *oic*. The polybasic acids are to be designated by the terminations *dioïc*, *trioïc*, *tetroïc*.

$CH_3—CO_2H$. Ethanoic acid.
$CO_2H—CH_2—CH_2—CO_2H$. Butane dioic acid.

27. In the case of the acids of the fatty series, carboxyl is to be considered as forming an integral part of the carbon chain.

28. The acids in which one or two atoms of sulphur displace as many atoms of oxygen of the carboxyl are to be named as follows:—The sulphur simply combined with the atom of carbon is to be denoted by *thiol*; if the connection be double, the particle thione is to be used.

$CH_3—CO—SH$. Ethane-thiolic acid.
$CH_3—CS—OH$. Ethane-thionic acid.
$CH_3—CS—SH$. Ethane-thione-thiolic acid.

29. In monobasic acids containing a normal or symmetric chain, the carbon of the carboxyl is to be numbered 1. In other cases the numbering of the corresponding hydrocarbons is to be retained.

$\overset{(4)}{CH_3}—\overset{(3)}{CH_2}—\overset{(2)}{CH_2}—\overset{(1)}{CO_2H}$.

$\overset{(1)}{CH_2}=\overset{(2)}{CH}—\overset{(3)}{CH_2}—\overset{(4)}{CO_2H}$.

$\overset{(1)}{CH_3}\diagdown\overset{(2)}{CH}—\overset{(3)}{CH_2}—\overset{(4)}{CO_2H}$.
$\overset{(2^1)}{CH_3}\diagup$

30. The present names for the salts and the compound ethers are to be retained.

31. The anhydrides are to retain, as at present, names derived from those of the corresponding acids (ethanoïc anhydride).

32. The lactones are to be designated by the suffix *olide*. The position in the principal chain occupied by the alcoholic oxygen with reference to the carbonyl may be expressed by the Greek letters α, β, γ, δ, and the customary numbering.

$CH_3—\underset{|}{CH}—CH_2—CH_2—\underset{|}{CO}—O$. Pentanolide, 1, 4,
or
γ Pentanolide, 1, 4.

The lactonic acids derived from bibasic acids are to be named like the lactones from which they are derived, with the addition of the termination *oic*.

$CO_2H—\underset{|}{CH}—CH_2—CH_2—\underset{|}{CO}—O$. Pentanolidoic acid, 1, 4.

33. *Amines*.—No change for the compound ammonias (ethylamine, ethylmethylamine, and ethene-diamine). When the group NH_2 is considered as a substituting group it is to be expressed by the prefix *amino*.

$NH_2—CH_2—CO_2H$. Amino-ethanoic acid.

Substances in which the bivalent group NH closes a chain composed of positive radicles are to be called *imines*:—

$CH_2\diagdown\ \diagup NH$. Ethene-imine.
$CH_2\diagup$

The Commission proposes to name the group NH_2 *amigenes*, and the group NH *imigenes*.

34. The nomenclature in use for the phosphines, arsines, stibines, sulphines is to be retained.

35. The derivatives of *hydroxylamine* formed by displacement of the hydrogen of the hydroxyl are to be designated by the suffix *hydroxylamine*.

$C_2H_5—O—NH_2$. Ethylhydroxylamine.

The oximes are to be denominated by adding the suffix *oxime* to the name of the corresponding hydrocarbon.

$CH_3—CH_2—CH_2—CH=NOH$. Butaneoxime 1.
$CH_3—CH_2—C(NOH)—CH_3$. Butaneoxime 2.

36. The names of *amides*, *imides*, *amidoximes* are to be retained.

$CH_3—CO—NH_2$. Ethaneamide.
$NH_2—CO\ CH_2—CH_2—CO—NH_2$. Butane diamide.
$NH_2\ CO—CH_2—CH_2—CO_2H$. Butane amidoic acid.
$CH_2—CO\diagdown\ \diagup NH$. Butaneimide.
$CH_2—CO\diagup$
$CH_3—C\overset{NOH}{\diagdown\!\diagup NH_2}$. Ethaneamidoxime.

37. The generic term *urea* is to be retained. It is to be employed as a suffix for the alcoholic derivatives of urea, whilst the acid substitution derivatives are to be known as *ureides*. Substances derived from two molecules of urea are to be designated by the suffixes *diurea*, *diureide*. The acid ureides are to take the name of ureic acids. The terminations uramic and uric are to be rejected.

38. *Amidines*.—This suffix is retained.

$CH_3—C\overset{NH}{\diagdown\!\diagup NH_2}$ Ethaneamidine.

39. The generic term *guanidine* is to be retained, but different guanidines are to be named as substituted derivatives of diamido-carbo-imidine.

40. *Betaïne*. Suffix *taine*.

$(CH_3)_3N——O$
$\quad\quad\quad

48. The name of the hydrazones is formed by replacing the termination *al* or *one* of the aldehydes and the ketones by the suffix *hydrazone*.

$CH_3—CH_2—CH=N—NH—C_6H_5$. Propane-hydrazone 1.

CH_3 / CH_3 >$C=N—NH—C_6H_5$. Propane-hydrazone 2.

The term *dihydrazone* is to be substituted for osazone.

49. The full discussion of the nomenclature of substances exhibiting complex functions was adjourned, and the study of this question remitted to the International Commission, so that it may prepare a project on this point which may be submitted to the next Congress. The Commission should endeavour to reconcile the demands of spoken nomenclature with those of a terminology suitable for dictionaries.

III.—*Radicles.*

50. The names of monovalent radicles derived from hydrocarbons by the elimination of an atom of hydrogen are to terminate in *yl*. This termination is to be substituted for the termination *ane* in the case of the radicles of the saturated hydrocarbons; it is to be added to the complete name of the hydrocarbon if this is not saturated.

$CH_3—CH_2$. Ethyl.
$CH_2=CH$. Ethenyl.
$CH\equiv C$. Ethinyl.

51. The radicles of alcoholic function, *i.e.*, those derived from alcohols by eliminating an atom of hydrogen united directly to carbon, are to be named by adding *ol* to the radicle of the corresponding hydrocarbon.

$—CH_2—CH_2OH$. Ethylol.
$—CH=CHOH$. Ethenylol.

52. The radicles of the aldehydes are to be named like those of the alcohols, putting *al* instead of *ol*.

$—CH_2—COH$. Ethylal.

53. The radicles of the acids which have retained the acid function, *i. e.*, which are derived from the corresponding acid by the elimination of an atom of hydrogen linked to the carbon, are to be named similarly, substituting *oic* for *al*.

$—CH_2—COOH$. Ethyloïc.

Those, on the contrary, which are derived from an acid by removal of a carboxylic hydroxyl are to be named by transforming the termination *oic* into *oyl*.

$CH_3—CO—$. Ethanoyl.

54. When two radicles are united to the same atom, the more complicated of them is mentioned first (phenylmethylhydrazine, pentylmethylamine).

IV. *Aromatic Series.*

55. In the case of aromatic derivatives, and in all substances containing a closed chain, all the lateral chains are considered as substitution groups.

$C_6H_5—CHO$.	Benzene methylal.
$C_6H_5—CH_2—CH_2OH$.	Benzene ethylol.
$C_6H_5—CO_2H$.	Benzene-carbonic acid (or carboxylic).
$C_5H_3N(CO_2H)_2$.	Pyridine dicarbonic acid (or dicarboxylic).

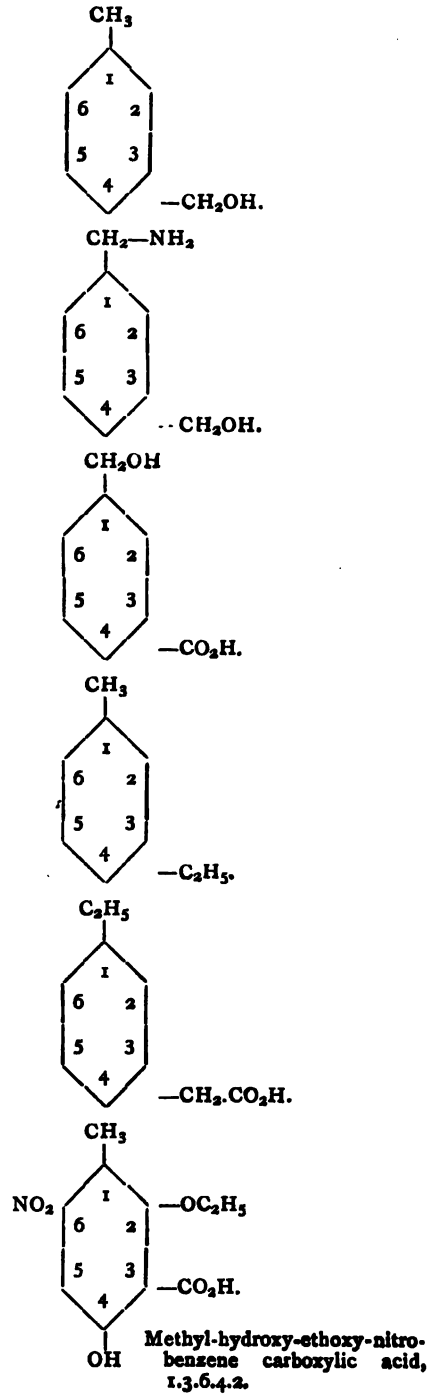
(The exigencies of language will decide which of these two last expressions is preferable).

56. The carbon atoms of the benzene nucleus and the lateral chains attached to it are to be numbered from 1 to 6.

57. In a poly-substituted derivative of benzene the index 1 is to be assigned to the substituting group in which the atom linked directly to the nucleus has the lowest atomic weight.

58. The place 1 being thus fixed, the indices of the groups are to be announced in the order of the increasing weights of the atoms directly linked to the nucleus. If two atoms linked to the nucleus are identical, the other atoms of the groups are to be taken into account, arranging them according to their atomic weights.

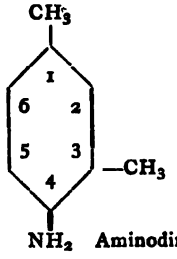
In case of several lateral chains, those are to be placed first which contain only a single atom of carbon. To classify these chains among themselves, it is to be considered whether they are derived from the group CH_3 by the



Methyl-hydroxy-ethoxy-nitro-benzene carboxylic acid, 1.3.6.4.2.

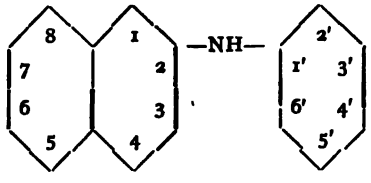
replacement of 1, 2, or 3 atoms of hydrogen, and in each of these categories the modification which involves the least increase of molecular weight is to come first; the chains with several atoms of carbon are to be classed respectively in an analogous matter.

59. If the same group occurs several times, in order to ascribe to index 1 that which will allot to the group of a different species next announced, the lowest index is to be adopted.



Aminodimethylbenzene, 1.3.4.

60. When two benzene nuclei are linked together directly or indirectly, the indices of the nucleus which follows last are to be accented.



Naphthylphenylamine, 2.1'.

61. The discussion on the nomenclature of substances containing non-saturated closed chains is adjourned until the publication of the ideas of Dr. Armstrong on this subject will enable the Commission to compare them with the proposals of M. Bouveault.

62. The Commission invites the editors of the leading chemical journals to come to an understanding on the application of the principles which it has adopted.

METHODS OF ANALYSIS OF DAIRY PRODUCTS.

Official Methods of Analysis of the Association of Official Agricultural Chemists for 1890-91.

(Continued from p. 270).

Estimation of Volatile Acids.

Reagents.

Solution of Caustic Soda.

1. 100 grms. NaOH dissolved in 100 c.c. pure water. The caustic soda should be as free as possible from carbonate, and be preserved from contact with the air.

2. Alcohol, about 95 per cent, re-distilled with caustic soda.

3. Solution of sulphuric acid containing 25 c.c. strongest H_2SO_4 in 1000 c.c. of water.

4. An accurately standardised approximately decinormal solution of barium hydrate.

5. Alcoholic solution of phenolphthalein.

Apparatus.

1. Saponification flasks of hard, well-annealed glass, capable of resisting the tension of alcohol vapour at 100° C. The flask shown in Fig. 3 is most suitable for this purpose. It should have from 250—300 c.c. capacity.

(*a*) Instead of such a flask an Erlenmeyer flask of the same capacity fitted with long glass tube or reflux condenser may be used.

2. A pipette graduated to deliver 40 c.c.

3. Distilling apparatus as represented in Fig. 4. One with a smaller bulb tube may also be used.

4. An accurately calibrated burette reading to tenths of a c.c.

The Manipulation.

Weighing the Fat.—The butter or fat to be examined should be melted and kept in a dry warm place at about 60° C. for two or three hours until the moisture and curd have entirely settled out. The clean supernatant fat is poured off and filtered through a dry filter paper in a jacketed filter containing boiling water, to remove all foreign matter and any traces of moisture. Should the filtered fat in a fused state not be perfectly clear the treatment above mentioned must be repeated.

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside, and heated for one hour to 100° C. (*circa*). The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within fifteen or twenty minutes of the time they are weighed. The weight of each flask is determined accurately, using a flask for a counterbalance or not, as may be convenient. The weight of the flasks having been accurately determined they are charged with the melted fat in the following way :—

A pipette with a long stem marked to deliver 5·75 c.c. is warmed to a temperature of about 50° C. The fat having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, it is taken up in the pipette, the nozzle of the pipette carried to near the bottom of the flask, it having been previously wiped to remove any adhering fat. The 5·75 c.c. of fat are allowed to flow into the flask and the pipette is removed. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand fifteen or twenty minutes, when they are again weighed.*

The Saponification.—10 c.c. of 95 per cent alcohol re-distilled from caustic soda are added to the fat in the flask, 2 c.c. of the concentrated soda solution are added, a soft cork stopper inserted in the flask, and tied down with a piece of twine. The saponification is then completed by placing the flasks upon the water or steam bath as indicated in Fig. 3. The flasks during the saponification, which should last for one hour, should be gently rotated from time to time, being careful not to project the soap for any distance up the sides of the flask. At the end of an hour the flasks, after having been cooled to near the room temperature, are opened.

Removal of the Alcohol.—The stoppers having been laid loosely in the mouth of the flasks, the alcohol is removed by dipping the flasks into a steam-bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause, or any creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapour may be removed from the flask by waving it briskly, mouth down, to and fro. Complete removal of the alcohol with the precautions above noted should take about forty-five minutes.

Dissolving the Soap.—After the removal of the alcohol

* Before weighing the flasks any desiccating material used in the balance should be removed. If round bottom flasks are employed, a special form of holder must be used. This is made on the principle of a test-tube rack, the lower board of the tray being perforated so as to receive the round bottom of the flask and being protected by lugs, so that on being placed on a table the bottoms of the flasks do not touch the table.

Example:

	Grms.
Weight of counterbalanced flask No. 3	22·5904
,, ,, ,, ,, No. 3+fat	27·6734
Weight of fat	5·0830

the soap should be dissolved by adding 100 c.c. of recently boiled distilled water, and warmed on the steam-bath with occasional shaking until the soap is completely dissolved.

Setting Free the Fatty Acids.—When the soap solution has cooled to about 60° or 70° C., the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid solution mentioned above.

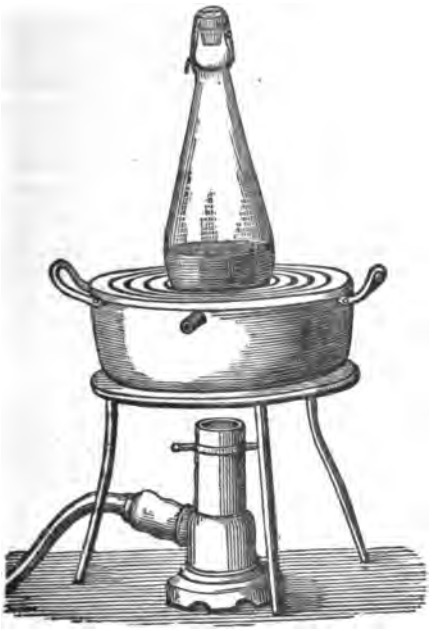


Fig. 3.

Melting the Fatty Acid Emulsion.—The flasks should now be re-stoppered as in the first instance, and the fatty acid emulsion melted by replacing the flasks on the steam bath. According to the nature of the fat examined the time required for the fusion of the fatty acid emulsions may vary from a few minutes to hours.

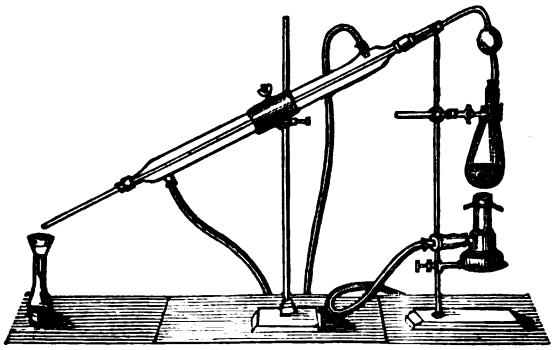


Fig. 4.

The Distillation.—After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flasks are cooled to room temperature and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at white heat, into distilled water, and keeping it under water until used. The flask is now connected with a condenser (Fig. 4), slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 c.c. of the distillate in as nearly as possible thirty minutes. The distillate should be receivep in flasks accurately graduated at 110 c.c.

Titration of the Volatile Acid.—The 110 c.c. of distillate, after thorough mixing, are filtered through perfectly dry filter paper and collected in a flask graduated at 100 c.c. The 100 c.c. of the filtered distillate are poured into a beaker holding from 200—250 c.c., 0·5 c.m. phenolphthalein solution added, and decinormal barium hydrate run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently unchanged for two or three minutes.

(To be continued.)

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 268).

Third Series.

It is only by gradual approach that very accurate quantitative work may be realised, and the earlier series were absolutely necessary as a training and preparation for the present one. This series had for its object not only an investigation of the effect of increased refinement, but also a definite proof that the amount of acid present in cupric sulphate was unaffected by the operations involved in the dehydration of the salt. To this end the first sample was not dehydrated at all, the second was heated only to 250°, and the third was exposed to the full heat of 365°, after the addition of sulphuric acid. Since the percentage of acid found in these samples did not vary beyond a reasonable limit of error, the proof is satisfactory.

The additional precautions taken in the preparation of the materials have already been mentioned under appropriate heads. Besides these, many refinements of manipulation were employed, too numerous to be fully described. For example, phosphorous pentoxide was used as a drying agent in the desiccator, and immediately after the introduction of a hot crucible the air was exhausted with a good air pump and re-admitted through a series of drying tubes. This method, of course, absolutely prevents the absorption of moisture by the contents of the crucible while cooling.

Again, in the ninth experiment, the solution of the perfectly neutral sodic sulphate was transferred to a small flask, heated to 103°, and evaporated by means of a current of pure dry air. When dry, the sulphate was gently ignited and weighed in the flask, and subsequently fused in a platinum crucible. The flask lost 0·00010 grm. during the operations, and the sodic sulphate lost 0·0003 grm. upon fusion. With the exception of the small flask, all the apparatus was of platinum. The sodic sulphate formed in the second experiment, and the sodic carbonate required in the third, were not determined.

The last experiment of the series was not of the same grade of refinement with the others. It is only included here because the same preparation of cupric sulphate was used in its execution.

The determination of the sulphuric acid by still another method was the object of this experiment. Baric sulphate was precipitated from a boiling solution of cupric sulphate strongly acidified with hydrochloric acid. After weighing as usual, the perfectly white precipitate was fused with

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Analysis of Cupric Sulphate.—Third Series: Data.

(Weights reduced to vacuum standard).

No. of Experiment.	$CuSO_4.5H_2O$ taken. Grms.	$CuSO_4$ found. Grms.	Metallic Cu found. Grms.	Na_2CO_3 found by methyl orange. Grms.	Na_2CO_3 found by phenolphthalein. Grms.	Sodic sulphate found. Grms.
7.	2·88307	—	0·73380	1·2242	1·22435	1·63994
8.	3·62913	2·32373 at 260°	0·92344	1·5407	1·54080	
9.	5·81352	3·71680 at 370°+	1·47926	—	—	3·30658
	$CuSO_4.5H_2O$ taken.		Baric sulphate found (uncor.).	Argentic chloride found.	Baric chloride calculated.	Baric sulphate corrected.
10.	3·1902		2·9967	0·0284	0·0206	2·9761

pure sodic carbonate, and the resulting cake thoroughly lixiviated with boiling water and dilute sodic carbonate solution. In the filtrate, the chlorine, which had been originally present as baric chloride occluded in the sulphate, was determined in the usual manner. Traces of baric sulphate and argentic chloride must have been dissolved in the wash water, but these errors tend to counterbalance one another, and hence no correction was made for them. Finally, the weight of baric chloride, calculated from the amount of chlorine found, was subtracted from the weight of baric sulphate; and from the corrected weight thus obtained the percentage of sulphuric acid in cupric sulphate was calculated. The astounding agreement of this experiment with the others may be nothing more than accident. In any case, the uncertainty of the atomic weight of barium, and the very unsatisfactory nature of baric sulphate, combine to make a repetition of the experiment of little value for the present purpose; but the method seems to be of value, and will form a subject of future investigation in this laboratory. It is well known that baric sulphate has great power of occluding many salts, but few experimenters seem to have realised that the occlusion of most metallic sulphates tends to *decrease* the amount of precipitate obtained. This fact was recognised by Professor Jannasch and the writer (*Jour. für Prakt. Chemie*, xxxix., 321) in 1889, and would influence the controversy between Ostwald ("Lehrbuch der Allgem. Chem.," i., 53) and Krüss (*Annalen*, cclxii., 40). The occlusion of baric chloride of course increases the amount of precipitate when sulphuric acid is to be determined, and diminishes it when barium is to be determined. With care this last error may be reduced to a very small amount, but it is doubtful if it has ever been wholly avoided. A trace only of copper was found in the precipitate obtained in the experiment described above, showing that cupric chloride is not occluded to any essential extent.

In spite of the fact that the important analyses of the third series were far more carefully performed than those of the second, the result was no more satisfactory than before. It was therefore apparent that a point had been reached beyond which further refinement was unavailing, and that the reason of the discrepancy must be sought, not in accidental or variable impurity, but rather in some property inherent in the purest cu pric sulphate,

Third Series: Results.

No. of Expt.	Water lost at 260°.	Water lost at 370°+.	Copper found.	SO_4 found from Na_2CO_3 (average).	SO_4 found. from Na_2SO_4.
7.	—	—	25·452	38·443	38·433
8.	35·970	—	25·446	38·435	
9.	—	36·067	25·445	—	38·431
					From baric sulphate.
10.					38·434
Average	35·970	36·067	25·448	38·439	38·433

Percentage Composition of Cupric Sulphate.

	Second Series.	Third Series.	Theoretical. Cu = 63·60.	Cu = 63·33.
Water	36·068	36·067	36·0695	36·109
Copper . ..	25·450	25·448	25·4665	25·385
SO_4	38·436	38·436	38·464	38·506
	99·954	99·951	100·000	100·000

(To be continued.)

A METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. BROWNING.

(Concluded from p. 272).

The next experiments were directed toward a separation of strontium and calcium nitrates. Definite amounts of a solution of strontium nitrate were measured from burettes into counterpoised beakers and weighed, as already described; the calcium nitrate was then added in solution, and the weight taken again. The water was evaporated, and the dry salts dissolved again in the least possible amount of water, and boiled with amyl alcohol (30 c.m.³) as before. The strontium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried, and weighed as previously described. The calcium was determined in the form of the sulphate by evaporation of the alcohol, treatment with an excess of sulphuric acid, and ignition.

Correction was made for the solubility of the strontium nitrate, and its consequent presence with the calcium, by calculating the amount dissolved in the portion of amyl alcohol employed to the condition of sulphate, and subtracting that quantity from the apparent amount of calcium sulphate found. The results of this mode of proceeding are recorded in experiments 10 and 11.

	SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
10.	0·0911	0·0932	0·0021 +	0·0932	0·0907	0·0025 −
11.	0·0915	0·0945	0·0030 +	0·0933	0·0899	0·0034 −

After making the correction in the manner specified, it is evident that the amount of strontium indicated is greater than that originally taken. It is apparent, therefore, that the strontium nitrate must have been contaminated, probably mechanically, by the calcium salt, as the calcium salt is found to be correspondingly deficient in amount. It was thought best, therefore, to have recourse to a double treatment with the alcohol. Accordingly, after the first boiling already described, the alcohol

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xliii., January, 1892.

carrying the greater part of the calcium in solution was decanted upon an asbestos felt under the conditions previously described, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, treated with a drop of nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30 c.m.³ of the alcohol were added, and the boiling repeated. The residue was filtered off upon the same felt through which the first portion had been decanted, and washed with amyl alcohol, care being taken to remove all particles of the residue from the beaker by careful rubbing. The crucible and residue were heated in an air-bath at 150° C. as before, and then weighed. The filtrate from the two treatments and the washings were treated differently in two series of experiments. In Series II. the filtrate was precipitated with sulphuric acid, ethyl alcohol being added to secure thorough mixture. The precipitated sulphate was filtered off upon asbestos, heated to low redness, and weighed. In Series III. the alcoholic filtrate was evaporated to a small volume, transferred to a weighed platinum crucible, and evaporated. The residue was ignited to burn off organic matter, treated with sulphuric acid, and again ignited at low redness and weighed.

Series II.

	SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
12.	0·1235	0·1239	0·0004 +	0·1290	0·1271	0·0019 −
13.	0·1237	0·1228	0·0009 −	0·1246	0·1226	0·0020 −
14.	0·1239	0·1239	0·0000	0·1248	0·1223	0·0025 −
15.	0·1974	0·1972	0·0002 −	0·0502	0·0492	0·0010 −
16.	0·1979	0·1978	0·0001 −	0·0496	0·0482	0·0014 −

Series III.

17.	0·0148	0·0155	0·0007 +	0·0256	0·0254	0·0002 −
18.	0·0183	0·0183	0·0000	0·1030	0·1015	0·0015 −
19.	0·0364	0·0366	0·0002 +	0·0516	0·0511	0·0005 −
20.	0·0365	0·0365	0·0000	0·0515	0·0513	0·0002 −
21.	0·0493	0·0494	0·0001 +	0·0515	0·0502	0·0013 −
22.	0·0497	0·0497	0·0000	0·0519	0·0511	0·0008 −
23.	0·0497	0·0503	0·0006 +	0·0249	0·0245	0·0004 −
24.	0·0729	0·0732	0·0003 +	0·0257	0·0251	0·0006 −
25.	0·0730	0·0732	0·0002 +	0·0255	0·0255	0·0000
26.	0·0744	0·0744	0·0000	0·0258	0·0260	0·0002 +
27.	0·0912	0·0910	0·0002 −	0·1286	0·1276	0·0010 −

The average error in the determination of strontium in both series is less than 0·0001 grm. + on the oxide; that of the calcium amounts to 0·0017 grm. − on the oxide in Series II., and to 0·0005 grm. − in Series III.

In both processes the correction for the solubility of strontium nitrate in amyl alcohol, determined as previously described, was applied—0·0020 grm. being added to the weight of the strontium oxide found after the double treatment with amyl alcohol, and 0·0035 grm. being deducted from the apparent weight of the calcium sulphate found before calculating it to the form of the oxide. The latter of the two processes, which are identical so far as handling of the strontium is concerned, yields the better results in the determination of the calcium, doubtless because a trifling amount of calcium sulphate remains in solution in the final filtrate in the former process, while in the latter every trace should be recovered. The deposition of minute traces of calcium in the precipitation of the strontium nitrate, to which reference has been previously made, is evidently a matter of no significance in comparison with the ordinary errors of manipulation.

Action of the Ethers of the Non-Saturated Acids upon Sodic Cyanacetic Ethers.—P. Th. Muller.—The author has examined the action of fumaric and citraconic ethers.—*Comptes Rendus*, cxiv., No. 21.

DETECTION OF THE HIGHER ALCOHOLS IN ETHYLIC ALCOHOL.

By M. C. BARDY.

THE author's method of operation is as follows:—Before all treatment we ascertain if the sample is rich in the higher alcohols or not. To this end we place in a tube 10 c.c. of the alcohol under examination with 100 c.c. of a standard solution of sodium chloride, agitate, and allow it to settle. Two cases may occur:—(*a*) the salt water retains the whole of the original liquid in solution; (*b*) an oily layer collects at the upper part of the tube. The course of procedure is the same in both cases, only the quantity of alcohol upon which we have to operate varies.

a.—The Brine does not Separate an Oily Liquid.

Take 100 c.c. of alcohol, introduce them into a large glass flask with a ground glass stopper at its upper part, and having a glass cock at its lower part, add 450 c.c. of a saturated solution of salt and then a quantity of pure water sufficient to re-dissolve the sodium chloride which is deposited (about 50 c.c.), introduce 60 to 70 c.c. of pure carbon disulphide, and shake briskly. Allow to settle for a few minutes and decant the sulphide into a flask like the former, but smaller (about 300 c.c.). Pour upon the milky liquid remaining in the large flask a further quantity of sulphide equal to the former. Shake up, decant, and repeat the treatment a third time, collecting in the smaller flask all the sulphides resulting from the exhaustion. If this treatment has been properly carried out the whole of the butylic and amylic alcohols will have been extracted by the sulphide.

To separate these alcohols add a quantity of concentrated sulphuric acid (about 2 c.c.), so that the yellow stratum formed by this acid may be more dense than the sulphide, and may easily reach the bottom of the flask. Agitate the mixture strongly, and then allow the acid to separate, assisting, if needful, the collection of the drops by giving the flask some shocks or some rotatory movements. Decant the acid into a small flask holding about 125 c.c. Repeat the acid treatment two or three times, using each time 1 c.c. of concentrated acid. Add these washing acids to the first acid collected, then heat the flask to 50° or 60° whilst passing a slight current of air over the surface of the liquid until all odour of carbon disulphide has disappeared. Add then a volume of glacial acetic acid almost equal to the volume of the sulphuric acid, and adapt to the neck of the flask a straight tube of one metre to serve as a refrigerant. Then heat the flask in a water-bath to about 100° for a quarter of an hour. When the etherification is complete remove the flask from the water-bath, and add to its contents 100 c.c. of brine. If the alcohol in question contains higher alcohols we see formed upon the surface of the liquid an oily layer of acetic ethers more or less abundant. To appreciate the volume of these ethers introduce the entire liquid into a flask of about 150 c.c. capacity, terminating at its lower part in a tube graduated in tenths of a c.c. and fitted with a cock.

Allow the oily layer to collect, decant the aqueous liquid by means of the cock in such a manner as to collect the ethers in the graduated part of the apparatus, plunge it into water at +15, and when an equilibrium of temperature has been obtained read off the volume of the oily stratum. The number read, multiplied by 0·8, gives the percentage of the butylic and amylic alcohols contained in the alcohol under examination.

b.—The Salt Water Separates an Oily Liquid.

As the alcohol in question contains in this case a large proportion of the higher alcohols, it is well to take only 25 c.c. as a sample and to add only 100 c.c. of brine and from 8 to 10 c.c. of pure water. The quantity of carbon disulphide does not need to be reduced, and the rest of the operation is effected as described in (*a*).

The carbon disulphide removes from the ethylic alcohol nothing except butylic and amylic alcohols; therefore, if the mixture contains propylic alcohol (normal or iso), this alcohol must be sought for in the liquid, which has been exhausted with carbon disulphide.

To this end the salty alcoholic liquid is distilled after having been first carefully filtered over moistened paper, and the product of the distillation is collected in a vessel containing an alcoholometer until this indicates 50°. At this moment the totality of the alcohol or of the alcohols has passed over. To find the proportion of propylic alcohol in this liquid two methods may be used. One of them, empirical, but generally sufficient, is the permanganate process of Barbet. The other, very accurate, is founded on Gossart's new process of homoetropy.—*Comptes Rendus*, cxiv., 1201.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.

Report to the Governors, April, 1892.

This report, which is presented by the council, must, we think, convince all who read it carefully that the Institute is not, as some persons are pleased to insinuate, a mere plaything for certain eminent persons, but that it has a very serious, well-defined object. For that object it is working earnestly and by no means unsuccessfully.

No inconsiderable number of young men who have studied at the various courses of the Institute are now filling honourable and useful appointments. Since 1887-8 the number of day students down to the winter term of 1891 has increased from 285 to 370. The students' fees last year were £4086 1s., as against £3772 6s. in 1890. Ten of the City Companies have come forward as benefactors to the Institute. The total income of the Institute for the year 1891 was £30,940 10s. 4d. Perhaps the least satisfactory of the Institute is the relatively small proportion of the chemical students. Thus, in the session ending in July, 1891, the day classes were attended only by 38 students out of a total of 185. In the evening classes there were 1240 students, of whom 99 only entered in the chemical department, the other departments having respectively 244 students (mechanical), 617 (electrical), 120 (applied art), and 160 (trade classes). This will be felt the more discouraging if we reflect that in the chemical arts we have comparatively the greatest difficulty in competing with our rivals.

It may be that the chemical arts and manufactures offer less remunerative positions than do the mechanical and especially the electrical trades. We should with all deference suggest that the Council of the Institute should make a careful investigation of the points in which its working agrees with, or differs from, those of the polytechnicums, *e.g.*, of Zurich and Aachen.

Detection of Fluorine in Bones Recent and Fossil.—Ad. Carnot.—In recent bones calcium fluoride is present in small proportions; 0·35 in a human thigh-bone, 0·45 in the thigh-bone of an ox, 0·63 in the thigh-bone of a sea-cow, and 0·20 in the tusk of an elephant. In fossil bones the proportion of fluorides is much larger. Thus the bones of a sea-cow from the deposits of Charlestown contained 6·21 calcium fluoride, the tusks of *Elephas Meridionalis* from the Pliocene of Saint-Prest 4·22, and the tusks of the mastodon of Simorre contain 5·30 per cent of calcium fluoride. The author is of opinion that this excess is due either to infiltrations containing traces of alkaline fluorides or to a slow transference of calcium fluoride derived from adjacent minerals.—*Comptes Rendus*, cxiv., No. 21.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 19th, 1892.

Prof. A. Crum Brown, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Arthur Edward Barrows, Bloomfield Iron Works, Tipton, Staffs.; Horatio Ballantyne, 269, Renfrew Street, Glasgow; Thomas Cockerill, 105, Derby Street, Bolton John Evans, Treas. R.S., Nash Mills, Hemel Hempstead; John Gibson, Ph.D., 15, Hartington Gardens, Edinburgh; Henry Ramsden Redman, 10, the Gardens, East Dulwich, S.E.

The President announced that the Council at their meeting that afternoon had adopted the following resolution expressive of the loss the Society and chemists generally had suffered by the death, on May 5, of Professor von Hofmann. The resolution would be communicated to the family of the deceased and to the German Chemical Society:—

The President and Council of the Chemical Society, at their first meeting since the death of their illustrious colleague Augustus William von Hofmann, desire to record their sense of his eminence and of the great scientific work he achieved both in England and in Germany.

Invited to London in 1845 to organise and superintend the Royal College of Chemistry, he spent nearly twenty years in this country, and during that time made many brilliant discoveries, and trained a body of investigators who have followed his example in extending the bounds of the science and in applying chemical principles to the industrial arts.

"Many of the Fellows of the Chemical Society were introduced by him to the science, and look back with gratitude to his inspiring teaching.

"Hofmann's influence on science in this country still remains, though the country of his birth has, since 1865, received the immediate benefit of his personal labours as an investigator, teacher, and organiser.

"The President and Council of the Chemical Society of London desire to express to their colleagues of the German Chemical Society their profound sorrow at the death of the great chemist so closely connected with both, and their sympathy with the sister Society in the loss of its distinguished President."

Of the following papers those marked * were read:—

*16. "*The Magnetic Rotation of Compounds supposed to contain Acetyl or of Ketonic Origin.*" By W. H. Perkin, Ph.D., F.R.S.

The author, after referring to the diverse views which are held as to the constitution of ethylic acetoacetate, draws attention to Bruhl's determination of the refractive powers of this substance, which favours a ketonic constitution, and to its magnetic rotation, which was determined several years ago by himself, and which also supports this view; a list is then given of seven acetyl compounds of which he has ascertained the magnetic rotations, all giving numbers pointing to a ketonic constitution. But as such compounds behave sometimes as ketonic and sometimes as hydroxy-derivatives, it was thought desirable to examine a larger number of compounds supposed to contain acetyl or of ketonic origin under different circumstances; the following were selected:—Pyruvic acid; levulinic acid, fused and in solution; ethylic acetonedicarboxylate; ethylic acetoacetate; acetylacetone; methylacetylacetone; ethylic β-amidocrotonate. The last-mentioned four were examined at widely different temperatures.

The rotation of the first five compounds gave numbers corresponding to a ketonic constitution, though those obtained with ethylic acetonedicarboxylate were rather

high, and it is therefore proposed to re-examine this substance at higher temperatures.

The rotation of acetylacetone was found to be very high, showing it to be an unsaturated or hydroxy-compound, whilst the value obtained for methylacetyl-acetone stands between the hydroxy- and ketonic rotations. At temperatures approaching that of boiling water, it was found, however, that these compounds give much lower rotations than when cold: in the case of the former, the values fall between the hydroxy- and the ketonic rotations, and in the case of the latter, they nearly correspond to the ketonic rotation, showing apparently that they change into the more stable or ketonic form when heated. The refractive and dispersive powers of the same compounds, determined at different temperatures, confirmed the magnetic rotations.

The magnetic rotatory power of ethylic β-amido-crotonate was found to be remarkably high, as was its refractive and dispersive power, showing it to be an unsaturated compound; the author proposes to continue the examination of substances of this class.

Discussion.

Dr. Collie remarked that he had long held the view that ethylic β-amidocrotonate was an imido-derivative, the correctness of which appeared to be demonstrated by Dr. Perkin's measurements.

Dr. Perkin, in answer to Dr. Morley, said that he had not yet ascertained whether acetone was abnormally affected by heating.

*17. "*The Origin of Colour. II. The Constitution of Coloured Nitro-compounds.*" By Henry E. Armstrong.

In a communication to the Society in March, 1888 (*Proceedings*, 1888, 27), in which the relation between colour and constitution was discussed, it was maintained that in the case of azo-dyes, the rosanilines, methylene-blue, &c., colour was conditioned by a *quinonoid* structure. Although the general correctness of this view has never yet been acknowledged, a study of the literature relating to coloured compounds which has appeared in the interval clearly shows that it is more and more recommending itself; it should also be mentioned that Nietzki, in the introduction to his *Organische Farbstoffe* (Berlin, 1889), makes reference to the quinonoid character of a number of dye-stuffs, although he does not seek to apply such a view of their structure at all generally. The subject has continually occupied my attention since I first brought it before the Society, and I think it is justifiable that I should now state the opinion at which I have arrived; viz., that in the case of coloured compounds which have been fairly well studied, it is so generally true that a quinonoid formula is applicable, that the reconsideration of the formula of any coloured substance is warrantable if it do not come within the rule. The term "*quinonoid*" must, however, be understood to include compounds of the type of benzyl; and it is to be noted that in the case of closed chain compounds, it appears to be essential that at least one of the quinonoid carbon atoms be associated with a dyad radicle, and that the ring itself be unsaturated: the presence of two ortho- or para-carbonyl groups in a saturated ring apparently does not condition colour.

Nitro-compounds have from an early period attracted my attention, as they do not come within the suggested "colour rule." It is well known, however, that nitro-compounds are not all coloured, many which are commonly described as yellow being obtained white when prepared from pure materials, and precaution is taken to remove the phenolic compounds which are so frequently formed even from hydrocarbons during nitration; from this it follows that the nitro-group does not *per se* condition colour. A comparison of ortho- with para-nitrophenol affords striking confirmation of the correctness of this conclusion: the former alone is coloured, being intensely yellow, very volatile, and insoluble in water; whereas paranitrophenol does not volatilise with steam, and is fairly soluble in water. To what is the difference ascribable? It can scarcely be otherwise than to a difference in structure beyond that involved in a mere difference in the relative positions of the radicles. Dr. Kipping and I, in the course of an investigation of coloured nitro-compounds in which we are engaged, have had occasion to compare the methoxynitrobenzenes prepared from ortho- and para-nitrophenol, and we find not only that they are *both* colourless, but that they agree as closely in their general properties as do most isomeric compounds containing the same radicles; it is particularly noteworthy that they are about equally volatile with steam. The non-correspondence of the two nitrophenols is rendered far more striking by the correspondence of the compounds prepared from them by methylation, and the conclusion is strengthened thereby that they are not mere position isomerides: it therefore appears justifiable to represent orthonitrophenol by a quinonoid formula, which may readily be done by transferring the hydroxylic hydrogen to the NO_2 group, thus transforming it into a dyad group, NO_2H, a change which admittedly attends the formation of so-called nitrosophenol (quinonehydroxime) (*cf.* Nietski, *op. cit.*, p. 9). On this hypothesis, the name *quinoneorthonitroxime* may be suggested for "orthonitrophenol."

Paranitrophenol, although itself colourless, yields coloured metallic derivatives, in the formation of which a change of structure must be involved, according to the view here advocated.

As only para- and ortho-compounds can have quinonoid formulæ, it would follow that metanitro-derivatives must be colourless; but actually metanitraniline has an intense yellow colour. There are but two ways out of this difficulty: to assume that metanitraniline either is not (as ordinarily obtained) an uniform substace, or that its structure is not really that of an amidonitrobenzene. There is, however, no obvious other mode of representing it; and although Dr. Kipping and I have spent much time in trying to deprive it of its colour, we have been unsuccessful; we have found, however, that it yields a practically colourless benzoate, a result which we regard as strong presumptive proof in favour of the view that metanitraniline is not what it is supposed to be, and we therefore propose to submit it and similar compounds to exhaustive study.

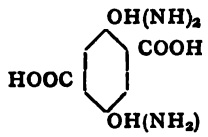
If it be granted that in the case of ortho- and para-nitrophenol there may be a transference of hydrogen or metal to the NO_2 group, leading to the formation of nitroximes, it is conceivable that a similar change may take place in other cases; for example, in the case of the primary nitroparaffins, the properties of which are in many respects compatible with the view that they are nitroximes. Moreover, the explanation would gain support which is afforded of the "acid" properties manifested by a compound such as benzyl cyanide, by regarding it as, at least potentially, an imide $C_6H_5.CH:C:NH$.

A consistent explanation of the formation of metallic derivatives could be given, and it would be unnecessary to assume that "hydrocarbon" hydrogen other than acetylenic is displaceable by metal, if the view here suggested were accepted.

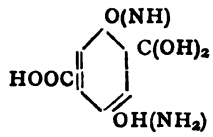
*18. "*The Origin of Colour. III. Colour as an Evidence of Isodynamic Change: the Existence of Isodynamic Acids.*" By Henry E. Armstrong.

The application of the colour-rule dwelt on in the foregoing note must lead not only to the modification of many of the formulæ attributed to coloured substances, but also to the recognition of equivalent or *isodynamic* forms (*cf.* Morley and Muir's "Watts' Dictionary of Chemistry," iii., Art. "Isomerism") of a variety of compounds, as I have already partially indicated. Thus it appears to me to be impossible any longer to regard the coloured substances known as paradihydroxyterephthalic acid, hihydroxypyromellithic acid and the corresponding "diamido-" acids (*cf.* Nef. *Annalen*, cxxxvii., 38) as con-

stituted in the manner suggested by these names, and there is no difficulty in representing them as quinonoid compounds, thereby accounting for their being coloured, thus:—



Dihydroxy-Diamido- } terephthalic acid.



Isodynamic form of Dihydroxy-Diamido- } terephthalic acid.

In principle this idea is not novel (*cf.* Hantzsch and Herrmann, *Ber.*, 1887, 2800; indeed, it has already been rejected (Baeyer, *Annalen*, ccxliv., 189; Nef, *ibid.*, cclviii., 261), but on grounds which I regard as altogether insufficient, holding, as I do, the opinion that the character of such substances is scarcely to be determined by purely chemical methods, owing to the readiness with which a change in type sets in. This is well illustrated in the case of the ethylic salts of "diamido-" terephthalic and pyromellithic acids, which are both red-coloured substances, but yield colourless salts with acids, the addition of HCl being sufficient, it would seem, to suppress the chromophoric group $C(NH)\cdot C(OH)(OEt)$, which becomes $C(NH_2\cdot HCl)\cdot COOEt$, so that in presence of acids such substances would tend to behave as amido-compounds.

If it be surmised on the evidence afforded by colour that acids exist which are not true carboxylic, but *carbhydrilic*, acids, there is no reason to deny the possible existence of such acids among colourless compounds, and it is conceivable that some of the reputed geometrically isomeric acids are of this character; von Baeyer's two hexahydroterephthalic acids perhaps afford an example of such isomerism. At present, however, we have no means of differentiating such acids from carboxylic acids.

There are a number of cases in which a suggestive explanation of peculiarities may be given with the aid of the hypothesis advocated in these notes. Thus, although orthonitromethoxybenzene is colourless when solid, the fused substance is yellow; if not due to the presence of impurity, or to slight decomposition, the appearance of colour in such a case may be conditioned by the occurrence of isodynamic change on heating. Then it is conceivable that the slight intensity in the colour exhibited by some substances may be due to the fact that the coloured and colourless isodynamic forms are both present, the coloured form in but small amount. On this view, it would be possible to understand the marked difference in intensity of colour sometimes apparent between derivatives of a coloured substance. Thus, in the case of the substituted nitrophenols, the silver derivative has frequently a much deeper colour than the potassium derivative; and the metallic derivatives of iododiorthonitrophenol are crimson, while those of the corresponding chloro-compound are bright-red; it may be that one metal more than another, and one halogen more than another, favours the occurrence of the isodynamic change on which the colour is dependent.

Discussion.

Dr. Armstrong, in reply to a remark by Professor Ramsay, said that although it was true that all substances exhibited absorptive power in some region of the spectrum, it was a remarkable fact that compounds which are coloured in the conventional sense clearly differ in constitution from colourless compounds, and it therefore appeared justifiable to discuss the origin of visible colour apart from the general question of absorption. If was very noteworthy that saturated compounds had but slight absorptive power even for invisible rays, and there appeared to be a connexion between the power of exercising selective absorption and what has been termed residual affinity: so much was this the case, that it appeared probable to him that ultimately colour would be traced to that peculiar condition represented conventionally by a double bond, the atoms being regarded as altogether subordinate.

(To be continued.)

NOTICES OF BOOKS.

Mineralogy. By F. H. Hatch, Ph.D., F.G.S. (of the Geological Survey of England and Wales). London: Whittaker and Co., and G. Bell and Sons, 1892. (Small 8vo., pp. 124).

In his preface the author notices the undeniable fact that mineralogy is now no longer in Britain at least a favourite pursuit. This present neglect is, he thinks, in part due to the predominant interest taken in biology. We are not sure that he is correct in his judgment. It seems to us that the declining popularity of mineralogy may be traced further back than the Darwinian avatar. In any case the science seems to find more cultivators in America and in France than in England.

Dr. Hatch has certainly done justice to his subject, and it is perhaps not too much to hope that his treatise may contribute to effect a revival of the study of mineralogy among us. The work is divided into two parts, the first treating of form, chemical composition, specific gravity, hardness, cleavage, fracture, and the optical phenomena of minerals: not, however, including double refraction and polarisation.

The second part is taken up with the classification and description of minerals. He seems to prefer a classification of minerals into rock-formers, ores, salts, and useful minerals other than ores, and lastly precious stones. Thus his arrangement is neither chemical nor crystallographic, but we might perhaps say utilitarian, which may possibly suit the tastes of the age. Among the useful minerals overlooked are bauxite, cryolite, and chrome iron. Some of the localities given would be improved by revision. Thus, as a locality for graphite, we find no mention of Ceylon. No locality is given for asbestos, which is merely tabulated among the hornblendes.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 21, May 23, 1892.

Combustion- and Formation-Heats of Alcohol, and of the Formic and Acetic Acids.—MM. Berthelot and Matignon.—This paper does not admit of useful abstraction.

Certain Facts concerning the Chemical History of Nickel.—P. Schutzenberger.—According to the most recent researches, the atomic weight of nickel seems definitely fixed at 58·6. An occlusion of oxygen is observed in a constant manner with nickel oxide calcined at white redness and finely pulverised. The greenish-yellow oxide, moderately calcined, does not present it, no more than does cobalt oxide strongly calcined. Reduced nickel obtained from the strongly calcined oxide, instead of becoming agglomerated under the influence of heat into a single mass of a metallic lustre, remains in the state of a dull, dark grey powder.

Soft Tempered Sulphur in the State of Vapour.—Jules Gal.—Sulphur, strongly heated, absorbs a certain quantity of heat, and passes into the insoluble state. A

similar absorption of heat, and a similar transformation, ought to ensue if the sulphur is evaporated, so that soft sulphur is obtained on receiving the vapours of sulphur on the surface of a cold liquid. The experiment succeeds equally well if we use as a tempering bath water, nitric acid, more or less dilute, hydrochloric acid, or a solution of soda, but it succeeds very badly with ammonia. The soft sulphur thus obtained has a peculiar aspect, in thin plates, and of a light yellow colour very different from the colour of ordinary sulphur. If examined with the microscope it appears formed of rounded grains, transparent, and cemented together in ramified reticulations. It is formed of a mixture of soluble and insoluble sulphur, but the insoluble sulphur extracted from it appears intermediate between those obtained from ordinary soft sulphur and from flowers of sulphur. If it is heated to 100° for one hour, 13·6 per cent remains in the insoluble state as compared with 0·3, the quantity obtained from ordinary soft sulphur, or 23, which is the yield from flowers of sulphur. The proportion of insoluble sulphur contained in soft sulphur, tempered in the state of vapour, varies with circumstances, especially with the temperature of evaporation. Below 200° it is very difficult to give numbers, for the vapour even if conducted by a gaseous current is inconsiderable, and the laminæ are formed very slowly. At higher temperatures the percentage of insoluble sulphur varies from 18 at 215°, to 37 at 320°.

Certain Basic Nitrates.—G. Rousseau and G. Tite.—Many basic salts have been prepared by heating the solutions of the corresponding neutral salts in sealed tubes in presence of an agent capable of saturating the free acid as it is separated, but the precipitates formed are often amorphous. To obtain crystalline deposits it is necessary to use not saline solutions but solid neutral hydrates whenever they are capable of undergoing aqueous fusion. The neutral nitrates examined have all behaved conformably to expectation except silver nitrate, which strongly attacks glass, forming a nitro-silicate. In all the experiments neutral hydroxides containing 6 mols. of water were heated to temperatures from 100° to 350°. Except in case of calcium nitrate where caustic lime was employed, the authors added small fragments of marble along with the solid hydrates. By operating in this manner the authors obtained basic nickel nitrate, $5NiO,N_2O_5,4H_2O$, basic zinc nitrate, $5ZnO,N_2O_56H_2O$, basic cadmium nitrate, $5CdO,2N_2O_58H_2O$, and a basic lime salt, $2CaON_2O_5,2H_2O$.

Preparation and Properties of Arsenic Cyanide.—E. Guenez.—The author causes cyanogen iodide to react upon free metallic arsenic. The compound obtained, $AsCy_3$, is a yellowish powder of a crystalline texture. It is decomposed instantly by water, which resolves it into arsenic and hydrocyanic acid.

Apocinchonine and Diapocinchonine.—E. Jungfleisch and E. Léger.—On heating cinchonine with hydrochloric acid of specific gravity 1·125 from 140° to 150° for 6 to 10 hours, Hesse obtained two bases which he described as apocinchonine and diapocinchonine. The authors find that diapocinchonine is a mixture and not a definite principle. The action of hydrochloric acid upon cinchonine produces the same isomers as that of sulphuric acid.

Monosodic Pyrocatechine.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

Substitutions Linked to Carbon and to Nitrogen. Application to Explosive Compounds.—C. Matignon.—Not suitable for abstraction.

Bibromomalonic Acid.—G. Massol.—Also a thermo-chemical paper not admitting of useful abstraction.

Detection of Higher Alcohols in Ethylic Alcohol.—C. Bardy.—(See p. 283).

On a Tetramethylmetadiamidobenzidine.—Charles Lauth.—Not adapted for abstraction.

Journal fur Praktische Chemie.
New Series, Vol. xlv., Parts 2 and 3.

Communication from the Chemical Laboratory of the Clark University, Worcester, Mass., U.S.A.—Massuo Skuta.—This memoir on the action of acet-acetic ether upon quinones, and on the synthesis of benzofurfuran derivatives seems to have already appeared in an English version.

Synthesis of Oxygenous Derivatives of Pyrazol.—L. Lederer.—This paper is chiefly devoted to a comparison of the reactions of antipyrin and isoantipyrin.

Determination of Sulphur in Inorganic Sulphides by Decomposition in a Current of Oxygen at a Red Heat, and Reception of the Products of Oxidation in a Solution of Hydrogen Peroxide. Analysis of Molybdenite, Realgar, and Orpiment.—P. Jannasch and V. Wasowicz.—This memoir will be inserted in full as early as possible.

(1) Simple Methods for the Quantitative Analysis of Galena. Analysis in the Moist Way by means of Bromine.—P. Jannasch and K. Aschoff.

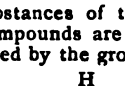
(2) Analysis of Galena in the Moist Way by Precipitating the Lead with Hydrogen Peroxide in an Ammoniacal Solution.—P. Jannasch and Th. Bickes.

(3) Analysis of Galena in the Dry Way by Ignition in a Current of Air Saturated with Bromine.—P. Jannasch and Th. Bickes.—These three methods will be given in full.

Communications from the Laboratory of Prof. Flawitsky, at Kasan.—These communications comprise a paper by F. Flawitsky on the "Dextrorotatory Terpene from the Needles of the Siberian Cedar" (*Pinus cembra*), and a memoir by B. Kuriloff on the "Terpenes from the Resin of *Pinus Abies*."

Introduction to an Accurate and Convenient Method of Determining Vapour Densities, even at Greatly Reduced Pressures.—C. Schall.—This memoir requires the three accompanying diagrams.

The First Stages of Reduction of the Nitro-group.—C. Willgerodt.—Substances of the first stage of reduction of the nitro-compounds are either dihydronitro-compounds distinguished by the group—



and the two nitroso-substances derived from them, in which the group $\leftarrow N=O$ is directly attached to the carbon, or products of condensation formed by the reduction of two nitro-mols. The compounds of the second stage of reduction may be simple or condensed. The author's relations with the German Chemical Society seem to be in an unpleasant state of tension.

Certain Salts of Hypophosphoric Acid.—C. Rammelsberg.—(This paper, though communicated by the author, has already appeared in the *Transactions of the Royal Prussian Academy of Sciences*). We have here an account of lithium hypophosphite, normal and acid, of thallium hypophosphite, normal and acid, and of the barium, magnesium, glucinum, silver, and lead salts.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xvii., No. 3.

This issue does not contain any chemical matter.

Series 3, Vol. xviii., No. 1.

The Borax of California.—From the Chem. News.

The Spontaneous Combustion of Coal.—From the *Proceedings of the British Association* at the Cardiff Meeting, 1891.

MISCELLANEOUS.

HIGH COURT OF JUSTICE.

TUESDAY, MAY 31, 1892.

QUEEN'S BENCH DIVISION.

Before the LORD CHIEF JUSTICE.

JOHNSTONE *v.* TILDEN AND OTHERS.

Mr. Jelf, Q.C., *Mr. Pocock*, and *Dr. B. O'Connor* (instructed by Mr. J. P. Godfrey) appeared for the Plaintiff.

The Solicitor-General (*Sir Edward Clarke*, Q.C.) and *Mr. Boydell Houghton* (instructed by Messrs. Markby, Stewart, and Co.), appeared for the Defendants.

(*Transcript from Shorthand Writer's Notes*).

The SOLICITOR-GENERAL—Will your Lordship forgive my interposing for the moment during the hearing of another case to relieve your Lordship's list of a case which we shall not have to trouble the jury with? It is the case of Johnstone *v.* Tilden and others, and my learned friend Mr. Jelf, who appears for the plaintiff, wishes to say a few words.

The LORD CHIEF JUSTICE—Certainly.

Mr. JELF—If your Lordship thinks that I am not unduly interfering with the case that is now on, to suit the Solicitor-General and my convenience, I should like to mention this case now. I appear for the plaintiff, Dr. Johnstone, with my learned friends Mr. Pocock and Dr. O'Connor. It is an action brought by the Doctor against the Institute of Chemistry of Great Britain and Ireland, represented here by my learned friend the Solicitor-General. The action was brought to prevent the Institute from persevering in excluding him from being a Member and Fellow of the Institute upon a certain charge of unprofessional conduct which had been made against him. My Lord, I have very carefully considered the facts, and the evidence on which this case was sought to be based, and although my client was very desirous of clearing his character as much as he possibly could, I pointed out to him that their Charter gave the Institute very large powers, so long as they were acting in good faith and in accordance with their rules, in deciding rightly or wrongly on the matters brought before them. My client has, I hope wisely, placed himself in my hands in the matter, and in accordance with what has passed between the Solicitor-General and myself, we have agreed, with your Lordship's permission, to deal with the case by making a short statement on each side. On the part of the plaintiff, I desire to withdraw unreservedly any suggestion that these gentlemen have been acting otherwise than in good faith and in accordance with the rules of the Institute. On the other hand, I am glad to say that the Solicitor-General sees his way to saying this on behalf of the gentlemen whom he represents: "That their action was founded entirely on their view of the professional conduct of the plaintiff on a single occasion, and involved no imputation upon his character or professional capacity." Two views might possibly be taken of the question that was at issue; but looking to the circumstances of the case, and, it seems to me, the very handsome way I have been met by the Solicitor-General, with the consent of his clients, I think it would be extremely unwise for my client to fight for more than he has received. Under these circumstances, we have agreed, with your Lordship's consent, to withdraw the record, and meanwhile the Plaintiff undertakes to give up any title he might have had to be a Fellow or Member of the Institute, and to hand over what perhaps I cannot say that my client is entitled to keep, but no doubt he will do what is right,—he will not persist in representing himself as a member of the Institute, and he will hand over his documents.

The SOLICITOR-GENERAL—I am much obliged to your Lordship for allowing me to interpose. Representing the authorities of the Institute of Chemistry, my only desire is to make it perfectly clear, and it is their only wish to make it clear, that they acted throughout deliberately and in the exercise of the deliberate judgment vested in them, and according to the Rules of the Institute to which the Plaintiff himself belonged. The words my learned friend has read are words that I agree to; I agree that there might be some controversy and difference of opinion as to the action of the Plaintiff himself, which was brought under the notice of the defendants, but it was carefully considered by them; they took the course they were bound to take in the interests of their profession, and I am glad to have the opportunity of saying not only that they have acted regularly in the manner, but they are anxious their action should not be taken to carry with it an imputation which it really ought not properly to bear. It was a question of professional conduct in a single instance and their action upon it, and that action they were obliged to notify. In this case, my Lord, we have agreed to the record being withdrawn with your Lordship's permission.

Mr. JELF—And no costs.

The LORD CHIEF JUSTICE—I can only give effect to the desire of the parties and the record may be withdrawn.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"The Chemist."—Mr. J. Cuthbert Welch will find full bibliographical details of "The Chemist" published in the CHEMICAL NEWS, vol. li., p. 304 (June 26, 1885). He will also find the dates of every volume of the same journal on p. 662 of my "Catalogue of Scientific and Technical Periodicals," published in the "Miscellaneous Collections of the Smithsonian Institution," (No. 514), Washington, 1885.—H. CARRINGTON BOLTON.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Chemical Industry, 8. "Oil-Gas," by Prof. V. B. Lewes. "The Soluble Bituminous Constituents of certain Japanese Coals," by Watson Smith.

TUESDAY, 14th.—Royal Medical and Chirurgical, 8.30.

WEDNESDAY, 15th.—Meteorological, 7.

——— Microscopical, 8.

THURSDAY, 16th.—Royal, 4.30.

——— Chemical, 8. Ballot for the Election of Fellows. "Contributions to an International System of Nomenclature—The Nomenclature of Cycloids," by Dr. H. E. Armstrong. "The Production of Pyridine Derivatives from the Lactone of Triacetic Acid," by Dr. N. Collie.

FRIDAY, 17th.—Quekett Club, 8.

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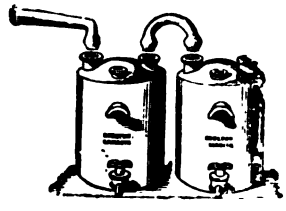

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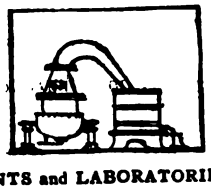

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THE CHEMICAL NEWS.

VOL. LXV., No. 1699.

THE QUALITATIVE DETECTION OF NICKEL AND COBALT.

By FRED. J. HAMBLY,
Assistant Lecturer and Senior Demonstrator in Chemistry, University College, Dundee.

THE qualitative detection of nickel in presence of cobalt is often a difficulty with the beginner in the study of analysis. When the conditions are correctly understood, Liebig's cyanide separation,—the essential details of which were fully worked out by Gauhe (*Zeit. für Anal. Chem.*, 1866, p. 75) in 1866,—is, in the writer's experience, the simplest and most rapidly executed. Although clearly stated by Fresenius in his "*Quantitative* Analysis,"* so far as I am aware, there is not one of all the multitude of text-books on qualitative analysis in our language which recommend this method that does not introduce some unnecessary condition into the procedure, and in most cases the student's difficulties arise not from his own incapacity, but from the faulty description given by his text-book.

Although the subject is not original, it may therefore be useful to call attention to the simplest and most satisfactory method of working. Gauhe showed conclusively that the conversion of potassium cobaltous cyanide into the cobalticyanide by boiling with hydrocyanic acid (at best a dangerous experiment), is always incomplete; but that by means of a suitable oxidising agent, in alkaline solution the cobalt may be directly converted into the soluble cobalticyanide, the nickel being simultaneously precipitated as hydrated nickelic oxide. The method of detecting nickel in presence of cobalt is then as follows. Separate the mixed sulphides from the ammonium sulphide precipitate by means of cold dilute hydrochloric acid, and test a small portion in a borax bead. The presence or absence of anything more than a trace of cobalt is directly indicated by the colouration produced. Dissolve the sulphides in hot hydrochloric acid with the aid of potassium chlorate, boil off the excess of chlorine, and remove the excess of acid either by neutralisation or evaporation to dryness. To the neutral solution add an excess of freshly prepared solution of potassium cyanide in cold water, *beyond* what is necessary to re-dissolve the precipitated cyanides. Boiling is unnecessary. Make the solution decidedly alkaline with sodium hydrate, add about twice the volume of bromine water, heat gently, allow to stand a few minutes, and filter off the precipitated nickelic oxide. The nickel may be confirmed by the borax bead reaction after washing the precipitate.

The action of the oxidising agent can be represented by equations, thus—

$$2KCN.Co(CN)_2+2KCN+Br=K_3Co(CN)_6+KBr.$$

$$2KCN.Ni(CN)_2+3NaOH+Br=$$
$$=Ni(OH)_3+NaBr+2KCN+2NaCN.$$

There is no liberation of hydrocyanic acid at any stage of the process, so the operations may be safely conducted in the open laboratory. Commercial cobalt salts almost invariably give a precipitate of nickelic oxide. The cyanide method has the advantage over the precipitation of the cobalt as potassium cobaltinitrite, in that the separation is most frequently carried out with the object of detecting *nickel*, which metal is immediately separated as a precipitate readily available for examination.

If the analysis is to include a search for traces of cobalt, the alkaline filtrate from the nickel precipitate is, *in the draught cupboard*, acidified with excess of sulphuric acid, and evaporated until the excess of acid is nearly expelled. The residue is taken up with water, made alkaline with ammonia, the cobalt, if present, precipitated by ammonium sulphide, and confirmed by the borax bead. Or, a portion of the neutral solution, containing the nickel, may be treated with acetic acid and potassium nitrite, and the traces of cobalt directly precipitated by allowing to stand for a few hours.

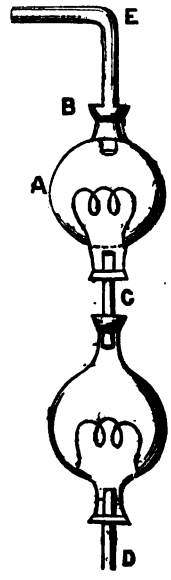
* Seventh English Edition, vol. i., p. 444. In his "Qualitative Analysis" Fresenius adopts the more tedious nitrite separation.

A NEW GASEOUS INCANDESCENT LAMP.

By H. N. WARREN, Research Analyst.

THE incandescent property of platinum in most of its allotropic modifications has been noted from an early period, but as regards brilliancy is far inferior to such substances as, for instance, magnesia, lime, asbestos, and lastly zirconia.

To thus obtain a suitable thread material in order to present a substance to work a filim from, probably no substance is better suited than asbestos itself, both on account of its indestructibility and also as regards its compactness and inferior conductibility of heat; but, on the other hand,



asbestos possesses none of the properties of platinum with respect to incandescence. True platinised asbestos prepared by immersing asbestos fibre in solution of platinic chloride has been, and still is, frequently employed to promote catalysis or surface action, but in comparing its value as a lighting agent it scores very low. In this case the decomposition of the platinum salt employed destroys by rendering rotten the fabric of the asbestos, and to overcome this difficulty the author has contrived and succeeded in combining a special combination of platinum not hitherto noted in conjunction with zirconia. The filim thus employed is mounted inside the small globe, as shown by the accompanying diagram, which represents two lamps, namely, A and B, which are readily connected to each other by the short tube, C, the bottom lamp, B, being connected at D with a gas supply arranged to admit of a supply of air and gas as through an ordinary Bunsen burner, the uppermost pipe, E, intended to convey

the waste gases through a suitable aperture into the open. The ignition of the filim is readily brought about by applying a heated wire during the passage of the gas, and provided the gas and air supply are kept constant, several such lamps may be fed from the one gas supply.

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REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg

(Continued rom p. 170).

IV.—*On the Uses of Steel.*

Besides making tool steel and casting chrome steel projectiles by the process worked out by the French workers, J. Holtzer, Unieux, Loire, we made steel for car and engine tyres for some Government special trains. We used a mixture of Beloretz puddled steel, cast-iron, and turnings resulting from the treatment of the projectiles in the mechanical shop.

Owing to this fact a certain quantity of chromium was always present in the steel for tyres. Ordinarily we had about 0·30 per cent of chromium in the metal. This quantity, however small, has a marked good influence on the metal, raising its tenacity. The test pieces taken out of the tyres gave on the average an elongation of 22—25 per cent in a length of eight inches.

The quantity of different elements in the tyre steel was as follows:—

Carbon (total)	0·45 per cent.
Manganese	0·18 ,,
Silicon	0·20 ,,
Sulphur	0·02 ,,
Phosphorus	0·03 ,,
Chromium	0·26 ,,

It is striking that such small quantities of chromium, as already observed by many engineers, produce such a good effect on steel, making the metal highly tenacious. A specimen tyre stood without cracking forty drops of a 15-pood monkey, being bent at last to the form of cipher 8.

The tool steel of the Poutiloff Iron and Steel Works is readily ordered by many railways and railway works. At the Works all the turning of hardened rolls, for their rail, beam, and plate trains is done by their own steel. The steel is made from a mixture of Beloretz puddled steel and cast iron, and contains about 1·25 per cent of carbon and 0·12 per cent of manganese.

Certain engineers advocate the use of large ingots for the manufacture of tool steel. They are hammered and rolled, and the resulting bars after inspection (flaws and cracks are chiselled out), are finished under quick working hammers down to the size demanded.

We used small ingots as mentioned in our previous paper; the same is done in most works abroad. It is easier to inspect a small ingot before sending it to the hammer, and next the evil of internal strains, which are constantly present in big ingots, is nearly avoided by the use of ingots of small dimensions.

In a further paper I propose to deal with the manufacture of projectiles in Russia. Several works here make capital artillery pieces, which were formerly obtained abroad.

METHODS OF ANALYSIS OF DAIRY PRODUCTS.

Official Methods of Analysis of the Association of Official Agricultural Chemists for 1890-91.

(Continued from p. 281).

Alternate Method of Determining Volatile Acids.

Saponification without the Use of Alcohol.

To avoid the danger of loss from the formation of ethers and the trouble of removing the alcohol after saponification, the fat may be saponified with a solution of caustic potash in a closed flask without alcohol. The operation is carried on exactly as indicated above for saponification in a closed flask, using caustic potash solution instead of soda, and omitting the operation for volatilising the alcohol. The caustic potash is prepared as follows:—Dissolve 100 grms. of the purest potassium hydrate in 58 grms. of hot distilled water. Allow to cool in a stoppered vessel, decant the clear caustic solution, and preserve in a vessel out of contact with the air. For the saponification use 2 c.c. of the caustic potash solution, which is poured on the fat after it has solidified in the flask. Great care must be taken that none of the fat is allowed to rise on the sides of the saponifying flask to a point where it can not be reached by the alkali. During the process of saponification the flask can only be very gently rotated in order to avoid the difficulty mentioned above. This process is not recommended in any except a closed flask with round bottom. In the subsequent solution of the soap, use only 80 c.c. of distilled water, and in setting free the fatty acids use 60 c.c. of the dilute sulphuric acid. In other respects the distillation is conducted as described. Potash is used instead of soda, so as to form a softer soap, and thus allow a more perfect saponification.

The saponification may also be conducted as follows:—The alkali and fat in the melted state are shaken vigorously in the saponification flask until a complete emulsion is secured. The rest of the operation is then conducted as above.

Iodine Equivalent.

Reagents.

1. Dissolve 25 grms. of pure iodine in 500 c.c. of 95 per cent alcohol. Dissolve 30 grms. of mercuric chloride in 500 c.c. of 95 per cent alcohol. The last solution, if necessary, is filtered, and then the two solutions mixed. The mixed solution should be allowed to stand twelve hours before using.

2. *Decinormal Hyposulphite of Sodium Solution.*—Take 24·6 grms. of chemically pure hyposulphite of soda freshly pulverised as finely as possible and dried between filter or blotting paper. Make this up to 1000 c.c. at the temperature at which the titrations are to be made.

3. *Starch Paste.*—One grm. of starch boiled in 200 c.c. of distilled water for ten minutes, and cooled to room temperature.

4. *Solution of Iodide of Potassium.*—150 grms. of iodide of potassium dissolved in water and made up to 1 litre.

5. *Solution of Bichromate of Potassium.*—Dissolve 3·874 grms. chemically pure bichromate of potassium in distilled water, and make the volume up to 1 litre at the temperature at which the titrations are to be made.

Manipulation.

Standardising the Hyposulphite of Sodium Solution.—Run 20 c.c. of the bichromate of potassium solution into a glass stoppered flask to which has been added 10 c.c. of the solution of iodide of potassium. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of hyposulphite of sodium to flow slowly into the flask until the yellow colour of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the hyposulphite of sodium solution until

the blue colour just disappears. The number of c.c. of hyposulphite solution used multiplied by 5 is equivalent to 1 grm. of iodine.

Example.—20 c.c. $K_2Cr_2O_7$ solution required 16·2 c.c. hyposulphite of soda; then $16·2 \times 5 = 81$ = number c.c. of hyposulphite solution equivalent to 1 grm. of iodine. Then 1 c.c. of hyposulphite solution = 0·0124 grm. of iodine. Theory for decinormal solution of hyposulphite of sodium, 1 c.c. = 0·0127 grm. of iodine.

Weighing the Sample.—About 1 grm. of butter fat is to be weighed in a glass stoppered flask holding about 300 c.c., with the precautions mentioned for weighing the fat for determining volatile acids.

Absorption of Iodine.—The fat in the flask is dissolved in 10 c.c. of chloroform. After complete solution has taken place, 30 c.c. of the iodine mercuric chloride solution are added. The flask is now placed in a dark place, and allowed to stand with occasional shaking for three hours.

Titration of the Unabsorbed Iodine.—100 c.c. of distilled water are added to the contents of the flask, together with 20 c.c. of the iodide of potassium solution. Any iodine which may be noticed upon the stopper of the flask should be washed back into the flask with the iodide of potassium solution. The excess of iodine is now oxidised with the hyposulphite of sodium solution, which is run in gradually with constant shaking until the yellow colour of the solution has almost disappeared. A few drops of starch paste are then added, and the titration continued until the blue colour has entirely disappeared. Toward the end of the reaction the flask should be stoppered and violently shaken, so that any iodine remaining in solution in the chloroform may be taken up by the iodide of potassium solution in the water. A sufficient quantity of hyposulphite of sodium solution should be added to prevent a reappearance of any blue colour in the flask for five minutes.

Setting the Value of the Iodine Solution by the Hyposulphite Solution.—At the time of adding the iodine solution to the fats, two blank flasks of the same size and nature as those used for the determination should be employed for conducting the operation described above without the presence of any fat. In every other respect the conduct of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used.

EXAMPLE.

Blank Determinations.

1. 30 c.c. iodine solution requires 46·4 c.c. hyposulphite of sodium solution.
2. 30 c.c. iodine solution requires 46·8 c.c. of hyposulphite of sodium solution.

Mean 46·6.

Percentage of Iodine Absorbed.

Weight of fat taken	1·0479 grms.
Quantity of iodine solution used	30 c.c.
Hyposulphite equivalent of iodine used ..	46·6 ,,
Hyposulphite to oxidise remaining iodine	14·7 ,,
Hyposulphite equivalent to iodine absorbed	31·9 ,,

Percentage of iodine absorbed, $31·9 \times 0·0124 \times 100 \div 1·0479 = 37·75$ per cent.

Elective Determinations.

For the further study of the properties of butter, the following recommendations are made, to be followed by the analyst or not as he may elect:—

Reduction of Silver.—To determine whether or not the butter has been derived from a cow fed on cotton-seed meal, it will usually be sufficient to test the sample by Bechi's reagent.

The solutions used are as follows:—5 grms. of silver nitrate dissolved in 100 c.c., 95 per cent alcohol, and 1 c.c. of strong nitric acid added. The manipulation is conducted as follows:—Measure out 5 c.c. of the fat into a small porcelain dish, and add 5 c.c. of the above reagent. Stir together thoroughly with a stirring rod, and place upon the steam-bath for ten minutes. Notice the changes of colour which take place, the intensity of the colour produced, and the amount of silver deposited as a mirror on the sides of the dish.

Reduction Test Applied to the Fatty Acids.—Instead of testing the original glycerides as above, the test may be applied to the fatty acids in accordance with the following directions:—

Reagent.—Dissolve 30 grms. of nitrate of silver in 100 c.c. of water.

Manipulation.—Place 5 c.c. of the fatty acid in the porcelain dish which is used above, and dissolve in 20 c.c. of 95 per cent alcohol. Add 2 c.c. of the reagent, stir thoroughly together, and heat on the water-bath as in the first instance.

Melting-point of the Fatty Acids.—The melting-point of the fatty acids may be determined as described in *Bulletin*, No. 13, Part 4, p. 448.

The melting-point of the fatty acids cannot be determined in the same apparatus and by the same methods as those described for the fats themselves, because the acids are soluble in alcohol. It should be remembered that the melting-point of the fatty acids is slightly above that of the glycerides, and the first determination in every case should be solely for the purpose of determining approximately the temperature at which the fat melts.

The bulb of a delicate thermometer is coated with the fatty acid, and the thermometer by means of a cork is fastened in a round flask of 250 c.c. capacity. The bulb of the instrument should occupy as nearly as possible the centre of the flask. The cork should have an air passage for the equalisation of the pressure. The flask is slowly heated in a current of warm air or otherwise, and as the melting-point is approached a rotary motion is given to it. When the fat melts it is seen to collect in a small drop on the lowest part of the bulb, remaining stationary while the flask is turned. The thermometer is best held horizontally.

Crystallising-point of the Fatty Acids.—The crystallising-point of the fatty acid is determined by means of the method described in *Bulletin*, No. 13, Part 4, p. 447.

A very delicate thermometer with a long bulb is used, the thermometer being graduated to tenths of a degree; the readings of the mercury are made with a small eye-glass. A test-tube about 15 c.m. in length and 2·5 to 3 c.m. in diameter is filled with the melted fatty acids. The temperature at which the acid is melted should be sufficiently high to secure a complete liquefaction. The tube containing the fat is placed in a stopper carried in a bottle so that the whole of the fatty acid may be contained in that part of the tube protected from external currents of air by the bottle. The bottom of this protected bottle should be warm, so that its temperature may be several degrees higher than the crystallising-point of the fatty acid. This precaution is necessary to avoid a too rapid crystallisation of the fatty acid in the bottom of the test-tube, and to secure as nearly as possible a uniform crystallisation throughout the whole mass. The thermometer is suspended in such a manner that the bulb may occupy as nearly as possible the centre of the fatty mass. The thermometer should be protected from currents of air, and should be kept perfectly still. The position of the mercury in the thermometer is carefully watched by the attendant as it gradually sinks toward the crystallising-point. When the crystals of the acid begin to appear in the bottom and on the sides of the test-tube, the descent of the mercury will become very slow and finally cease. The lowest point reached by the mercury should be noted. As the crystallisation extends inward towards the bulb of the thermometer a point will be reached when the mercury will begin to rise. At that point, the test-tube being held by the left hand, the thermometer should be taken by the right hand of the operator, and the partially crystallised mass of fat thoroughly stirred by turning the thermometer

three or four times around the tube in both directions. Care should be exercised that at the end of this operation the bulb of the thermometer should hang as near as possible in the centre of the crystallising mass. Directly the above operation is accomplished the mercury will be seen to rise, and this rise of temperature will continue for some time, after which the mercury will remain stationary

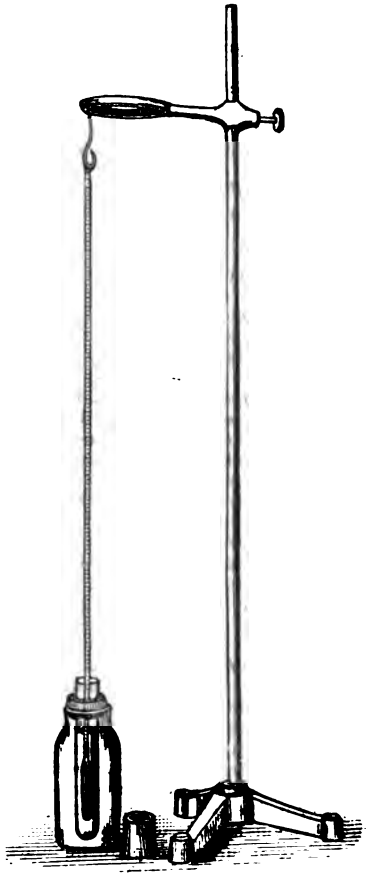


Fig. 5.

for one or two minutes. The highest point reached is taken as the true temperature of crystallisation.

Refractive Index.—The refractive index is conveniently determined by the apparatus of Professor Abbe, Fig. 6. The manipulation is conducted as follows:—Fine tissue paper or rather heavy body is cut into rectangular pieces 3 c.m. in length by 1·5 c.m. in breadth. One of these pieces of paper is placed on the lower of the two glass prisms of the apparatus. Two or three drops of the oil or fat are placed upon the paper and the upper prism carefully placed in position so as not to move the paper from its place. In charging the apparatus with the oil in this way, it is placed in the horizontal position. After the paper disc holding the fat is secured by replacing the upper prism, the apparatus is placed in its normal position and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus is now turned until the rainbow colours on the part between the dark and light field have disappeared. Before doing this, however, the telescope, the eyepiece of the apparatus, is so adjusted as to bring the cross lines of the field of vision distinctly into focus. The index of the apparatus is now moved back and forth until the dark edge of the field of vision falls exactly in the intersection of the cross lines. The refractive index of the fat under examination is then read directly upon the scale by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus should be turned through an angle of 180° until the colours have again disappeared, and the scale of the instrument again read. These two readings should fall closely together, and their mean is the true reading of the fat under examination.

For butter fats the apparatus should be kept in a warm place, the temperature of which does not fall below 30° C. For reducing the results obtained to a standard temperature, say 25° C., the following factor may be used. The

Fig. 6.

mean rate of variation in the refractive index of butter fats for each degree of temperature was determined by me in twelve samples of butter fat (see *Journal of Analytical Chemistry*, ii., Part 3, July, 1888). This factor is 0·000176. As the temperature rises the refractive index falls.

Example.

Refractive index of a butter fat determined at 32° 4 = 1·4540, reduced to 25° C., as follows:—32·4 − 25 = 7·4 = 0·0013; then 1·4540 + 0·0013 = 1·4553.

The instrument used should be set with distilled water at 25° C., the theoretical refractive index of water at that temperature being 1·3330. In the determination above given the refractive index of pure water measured 1·3300; hence the above numbers should be corrected for theory by the addition of 0·0030, making the corrected index of the butter fat mentioned at the temperature given, 1·4583.

Soluble and Insoluble Acids.—Use method described in *Bulletin* 13, Part 4, pages 455 to 461.

Saponification Equivalent.—Use method described in *Bulletin* 13, Part 4, pages 461, 462.

Rise of Temperature with Sulphuric Acid.—Use method described in *Bulletin* 13, Part 4, pages 443 to 446.

Decomposition of Ammoniacal Phosphorus Pentachloride by Heat. Phosphorus Chloronitride and Phospham.—A. Besson.—In 1890 the author indicated the existence of a compound $PCl_5 8NH_3$. If this substance is gently heated it loses ammonia. By the action of heat we obtain a chloronitride, $(PCl_2N)_3$, and finally a greyish white solid body, phospham, PN_2H. Under the continued action of heat the phospham is gradually destroyed, with loss of nitrogen and hydrogen.—*Comptes Rendus*, cxiv., No. 22.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 282).

The Cause of the Deficiency.

It was by no means easy to trace the cause of the disappearance of less than one two-thousandth part of the material to its true source.

The notable agreement between the percentages of water given in the first three columns of figures immediately above of course suggested the possibility of a loss of copper and sulphuric acid during the electrolysis; and it became an important matter to test the point.

Accordingly weighed portions of a dilute solution of pure sulphuric acid were estimated with weighed amounts of sodic carbonate. Other portions of the same solution, weighed alternately with the previous ones, were then evaporated over the water-bath with small amounts of cupric nitrate and successive additions of water. The cupric sulphate formed by this treatment was wholly decomposed by electrolysis, and the resulting sulphuric acid was determined exactly in the usual manner. The comparison of the acid solution before and after electrolysis is capable of showing at once whether any sulphuric acid was mechanically or chemically lost during the process. If any nitric acid had been held by the sulphuric acid in the second case, it could not have escaped decomposition during the electrolysis.

Following are the results:—

Strength of H_2SO_4 before Electrolysis.

(Weights reduced to vacuum.)

No. of Exp.	Solution taken. Grms.	Na_2CO_3 required. Grms.	Na_2CO_3 for 10·000 grms. solution. Grms.
11.	5·5932	1·0175	1·81917
12.	11·4175	2·0768	1·81896
		Average	1·81906

Strength of H_2SO_4 after Electrolysis.

(Weights reduced to vacuum.)

13.	16·8214	3·0592	1·81865
14.	5·5612	1·0115	1·81886
		Average	1·81876

Difference between averages 0·0003.

Known mishaps tended to make the first experiments of each of the two groups respectively too high and too low. It is seen that the second experiments gave nearly identical results. Considering the increased transference and manipulation involved in the second group, the conclusion seems to be warranted that little, if any, sulphuric acid is lost during electrolysis.

In order to prove like relations with regard to copper a similar method was adopted. Weighed amounts of electrolytic copper were dissolved in pure nitric acid in a flask provided with bulb tubes for the condensation of spray. The cupric nitrate was then evaporated with an excess of sulphuric acid upon the water-bath, and the cupric sulphate was electrolysed as usual.

Electrolysis of Copper.

No. of Ex.	Copper taken. Grms.	Copper found. Grms.	Loss of Metal. Grms.
15.	1·24156	1·24139	0·00017
16.	1·00613	1·00600	0·00013

Here again, the manipulation was so much more elaborate than in a simple electrolysis that it is difficult to decide where the slight loss took place. In another experiment (No. 17) both copper and sulphuric acid were weighed before and afterward, but the experimental operations were so doubly involved that the determination was of very doubtful value. The result was not materially different from the others, however. The significant portions of the data will be given later on.

In the course of these experiments it was found that a compact and brilliant copper film may be safely washed by decantation if sulphuric acid alone is present. Indeed, during most of the preceding determinations this method was adopted to insure complete collection of the acid, and in only one case (experiment 7) was as much as one twentieth of a m.grm. of copper found in the filtrate. In this case that amount was added to the larger quantity, and the sum is given in the table. Potassic ferrocyanide was the reagent used in the colorimetric tests.

Assuming the deficiency of copper and acid as found above to represent a real loss during electrolysis, the composition of cupric sulphate would be:—

	Uncorrected.	Corrected.
Water	36·067	36·067
Copper	25·449	25·452
SO_4	38·435	38·442
	99·951	99·961

That is to say, an undoubtedly excessive value for this correction would account for only one-fifth of the deficiency for which explanation was sought. The correction is at best very doubtful, and it is not applied in the final calculation of the atomic weight. Its application would make no essential difference in the final result, but would render the individual variations much less marked.

The only probable interpretation of the deficiency now lay in the assumption that cupric sulphate still held a volatile impurity at 360°. Such an amount of any non-volatile foreign substance would have increased the weight of sodic sulphate found at the conclusion of the analysis by about eight one-hundredths of one per cent, an amount entirely too large to escape detection. Besides, such a source of error has already been shown to be unlikely.

After it had been experimentally proved that cupric sulphate had no tendency to hold ammonic sulphate at 370°, the hypothesis of the occlusion of a small amount of water became the last resource. At first sight it seems improbable that any material could hold appreciable quantities of water in the presence of sulphuric acid when so strongly heated. But it must be remembered that at this temperature the acid is dissociated, and water is actually present in the vapour. It was hoped that sulphur trioxide might be more efficient as a dehydrating agent but a single experiment (No. 18) showed that cupric sulphate possessed more affinity for water, even at 300°, than did the sulphur trioxide. 2·3787 grms. (in vacuum) of cupric sulphate lost 0·8554 grm. in weight on heating to about 300° in a glass tube under a current of dry air. Upon continuing the application of heat in air charged with sulphuric anhydride from Nordhausen acid, no essential change in weight was observed. The apparatus was somewhat complicated in order to avoid rubber connections, but a description of it is superfluous. The total loss was 35·962 per cent of the weight taken.

Experiments showed that between 360° and 400° cupric sulphate does not essentially lose in weight. For example (No. 19 or 23), 1·28563 grms. of the substance dried at the former temperature weighed 1·28558 grms. after heating for ten hours at 400°. At the temperature of dull redness the salt slowly decomposes.

(To be continued).

* Contributions from the Chemical Laboratory of Harvard College, From the *Proceedings of the American Academy of Arts and Sciences.* vol. xxvi.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 19th, 1892.

(Concluded from p. 286).

Prof. A. Crum Brown, F.R.S., President, in the Chair.

*19. "*Studies on Isomeric Change.* No. IV. *Halogen Derivatives of Quinone.*" Part I. By Arthur R. Ling.

Dichlorobromophenol [OH : Cl_2 : Br = 1 : 2 : 6 : 4], prepared from parabromophenol and sulphuryl chloride, crystallises from light petroleum in silky needles melting at 66·5°; it gives metadichloroquinone when treated cold with nitric acid (1·5), and a mixture of dichloroparanitrophenol (m. p. 125°) and chlororthoparadinitrophenol (m. p. 110—111°) when warmed with nitric acid in glacial acetic acid solution.

Metachlorobromoquinone [O_2 : Cl : Br = 1 : 4 : 2 : 6], prepared by adding chlorodibromophenol—

[OH : Cl : Br_2 = 1 : 2 : 4 : 6]

to cooled nitric acid (1·5), crystallises from alcohol in yellow needles melting at 114—115°. The quinol melts at 154—155°.

Paradichlorobromoquinone [O_2 : Cl_2 : Br = 1 : 4 : 2 : 5 : 6], obtained by brominating paradichloroquinone (m. p. 161°), melts at 160—161°. The *quinol* crystallises from water in monohydrated needles melting at 124—126°; the anhydrous substance melts at 135·5°. The diacetyl derivative melts at 158—159°.

Metadibromochloroquinone [O_2 : Cl_2 : Br = 1 : 4 : 2 : 6 : 5], produced by brominating metadichloroquinone (m. p. 121°), melts at 168°. The quinol crystallises from water in anhydrous needles melting at 135°, its diacetyl derivative melting at 173—174°.

Paradichloroquinone does not yield metadichlorodibromoquinone on bromination, as stated by Hantzsch and Schniter, but the normal product—paradichlorodibromoquinone — is obtained. *Paradichlorodibromoquinone* [O_2 : Cl_2 : Br_2 = 1 : 4 : 2 : 6 : 3 : 5], produced in this way, forms six-sided plates melting at 292°; the *quinol* melts at 235—236°, its *diacetyl* derivative melting at 269—270°. The quinone does not yield chlorobromanilic acid on treatment with alkali, as Levy has stated, but a compound consisting of 1 mol. proportion of chloranilate and 2 mol. proportions of bromanilate. It is then shown that metadichloroquinone yields paradichlorodibromoquinone, identical in all respects with the last mentioned, when it is brominated in boiling glacial acetic acid solution; when, however, the bromination is conducted at the ordinary temperature, the product consists chiefly of the normal product, metadichlorodibromoquinone.

Metadichlorodibromoquinone—

[O_2 : Cl_2 : Br_2 = 1 : 4 : 2 : 6 : 3 : 5]

is obtained exclusively when metadichlorobromoquinol (m. p. 135°) is suspended in carbon tetrachloride and heated in a closed bottle in a bath of boiling water, and the product oxidised; it crystallises from benzene in six-sided plates melting at 291°; the corresponding quinol melts at 231—232°, its diacetyl derivative melting at 265—266°. The quinone yields chlorobromanilic acid on heating it with alkali.

*20. "*Halogen Derivatives of Quinone.*" Part II. By Arthur R. Ling and Julian L. Baker.

Chlorotribromoquinone, prepared by brominating m nochloroquinol in acetic acid solution, and subsequently oxidising, crystallises from benzene in yellow, six-sided plates, and melts at 292°.

The formation of chlorobromanilic acid on treatment with alkali, as previously stated by one of the authors, was only observed in one experiment; in all others the *molecular compound*,—

$C_6ClBr(ONa)_2O_2 + 2C_6Br_2(ONa)_2O_2 + 12H_2O$,

was obtained. Chlorotribromoquinol crystallises from benzene in small colourless needles melting at 233—234°; the diacetyl derivative separates from benzene in needles melting at 275°.

Trichlorobromoquinone is obtained by brominating trichloroquinone; it separates from benzene in yellow six-sided plates and melts at 289—290°. On treatment with soda, it yields the *compound*—

$C_6Cl_2(ONa)_2O_2 + 2C_6ClBr(ONa)_2O_2 + 10\frac{1}{2}H_2O$.

The formation of chlorobromanilic acid, as stated by Levy and Schultz, was not observed. Trichlorobromoquinol, prepared by reducing the quinone, crystallises from benzene in flat needles melting at 230—231°, its *diacetyl derivative* crystallising from acetic acid in colourless needles melting at 261—262°. The authors draw attention to the fact that in the interaction of the tetrahalogen quinone and alkali at least 3 mols. of the quinone appear to be simultaneously concerned (compare also preceding abstract).

*21. "*The Crystalline Forms of the Sodium Derivatives of Substituted Anilic Acids.*" By William J. Pope.

A comparison of the crystallographic dimensions of the sodium of the brominated and chlorinated anilic acids referred to in the preceding abstracts shows that the crystals possess considerable similarity. The salts examined crystallise in the anorthic system and have the following axial relations:—

Sodium bromanilate, $C_6(ONa)_2Br_2O_2,4H_2O$, $a : b : c$ = 0·8768 : 1 : 0·8100; α = 69° 28′; β = 87° 56′; γ = 71° 49′.

Sodium chloranilate, $C_6(ONa)_2Cl_2O_2,4H_2O$, $a : b : c$ = 0·8743 : 1 : ?; α = 88° 8′; β = 89° 51′; γ = 72° 30′.

Sodium chlorobromanilate, $C_6(ONa)_2ClBrO_2,4H_2O$, $a : b : c$ = 0·888 : 1 : 0·814; α = 69° 59′; β = 87° 3′; γ = 71° 58′.

A double salt, composed of 2 mol. proportions of sodium bromanilate and 1 of sodium chloranilate, having the composition—

$2C_6(ONa)_2Br_2O_2,4H_2O$; $C_6(ONa)_2Cl_2O_2,4H_2O$,

is obtained by the action of caustic soda on paradichlorodibromoquinone and crystallises in the anorthic system. It possesses the constants $a : b : c$ = 0·8825 : 1 : 0·8163; α = 69° 48′; β = 87° 14′; γ = 72° 11′. The same double salt, prepared by simply crystallising a mixture of the two constituents in the requisite proportions, gives numbers practically the same as these:—$a : b : c$ = 0·8825 : 1 : 0·8143; α = 69° 56′; β = 87° 7′; γ = 72° 11′. The identity of the two samples of double salt prepared in different ways is thus established. The crystals of the above substances consist of small distorted prisms exhibiting the forms $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{1\bar{1}0\}$, and $m\{\bar{1}01\}$. The form $m\{\bar{1}01\}$ is not met with on crystals of sodium chloranilate, so that the axial ratio $b : c$ is in this case indeterminate. It is to be remarked that the chloranilate differs considerably in angular dimensions from the salts containing bromine, which approximate very closely to one another in geometrical properties. The crystals of these salts nearly always show a curious step-like structure, which extends in the direction of the c axis and frequently obliterates the forms $m\{\bar{1}01\}$ and $c\{001\}$ at the end of the crystal. A noteworthy fact is the great resemblance between the simple salts and the double salt of sodium brom- and chlor-anilate. The crystals of all the above-mentioned substances are, under ordinary conditions, opaque, but, when crushed to powder and examined microscopically, are seen to transmit light of a claret colour.

22. "*Formation of a Hydrocarbon*, $C_{18}H_{12}$, *from Phenylpropionic Acid.*" By F. Stanley Kipping, Ph.D., D.Sc.

Having studied the action of phosphoric anhydride on a number of fatty acids (*Chem. Soc. Trans.*, 1890, 532, 980), it appeared desirable to ascertain whether benzenoid

acids would yield ketones under similar conditions; phenylpropionic acid was chosen. When this acid is heated with phosphoric anhydride, a reddish brown resinous mass is obtained; from this product I have so far succeeded in isolating three compounds, but others are doubtless formed.

1. A *hydrocarbon*, which after re-crystallisation from boiling xylene, gave on analysis results corresponding to the formula C_3H_2, 0·1515 grm. substance yielding 0·5250 grm. CO_2 = 94·51 per cent carbon, and 0·0710 grm. H_2O = 5·21 per cent hydrogen; the calculated values are carbon 94·74, hydrogen 5·26 per cent.

The hydrocarbon crystallises in pale yellow plates, does not melt at 250°, and is insoluble in most ordinary solvents, and only very sparingly soluble in boiling xylene; it is evident from its properties that it has a high molecular weight, its molecular formula being probably $C_{18}H_{12}$. It dissolves in hot, concentrated sulphuric acid, yielding a sulphonic acid which is readily soluble in water. On prolonged boiling with a mixture of potassium bichromate and sulphuric acid the hydrocarbon is converted into a deep yellow or orange compound; this substance is doubtless a *quinone* of the composition $C_{18}H_{10}O_2$, but as it is insoluble in all the ordinary solvents, and only very sparingly soluble in such liquids as boiling xylene, &c., it is not easily obtained in a pure condition; analyses gave about 1 per cent of carbon too much, probably owing to the presence of unchanged hydrocarbon. A *dibromo*-derivative of the composition $C_{18}H_{10}Br_2$ is formed when the hydrocarbon is treated with bromine; this substance crystallises from boiling xylene in microscopic needles, and does not melt at 300°.

2. The second compound which is formed by the interaction of phosphoric anhydride and phenylpropionic acid is of greater interest than the hydrocarbon; it is, however, produced in such small quantities that up to the present I have only obtained its hydrazone in a pure condition. This *hydrazone* crystallises from dilute alcohol in yellow needles, melts at 127—128° with decomposition, and on analysis gives results agreeing well with those required by a compound of the composition $C_{15}H_{14}N_2$; when heated with concentrated hydrochloric acid it is converted into a colourless, crystalline compound, which melts at about 245°, is insoluble in water, and contains nitrogen. The constitution of the ketone (or aldehyde) from which this hydrazone is derived is, of course, at present quite a matter of speculation, but is possibly represented by the formula—

$$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH_2.$$

This view is supported by the fact that, by treating phenylpropionic acid with phosphorus pentachloride in order to convert it into the chloride $CH_2Ph{\cdot}CH_2{\cdot}COCl$, and then warming an ethereal solution of this chloride with aluminium chloride, I obtained an oil which is insoluble in sodium carbonate, and which gives with phenylhydrazine a hydrazone identical with that described above.

3. The third product obtained by the action of phosphoric anhydride on phenylpropionic acid seems to be an organic derivative of phosphoric acid.

The experiments here described are still very incomplete, but it appears desirable to call attention to them as, if ketohydrindene derivatives are really produced in this way, their investigation cannot fail to be of interest.

23. "*Metallic Derivatives of Acetylene.*" By R. T. PLIMPTON, Ph.D.

A report in the CHEMICAL NEWS (lxv., 169) of a preliminary paper read by Dr. Kaiser before the Chemical Section of the Franklin Institute, on the copper and silver compounds of acetylene, leads me to publish some of the results of an investigation of these and other metallic derivatives with which I have been engaged for some time past.

I.—*Silver Compounds.*

Silver Nitrate and Ammonia.—The precipitate formed by acetylene in ammoniacal silver nitrate is in dilute solutions (decinormal) bright yellow; in strong solutions the yellow, curdy substance first thrown down is prone to pass into a white and less bulky form. The yellow substance often undergoes the same change when allowed to stand under water containing acetylene and protected from light. The white substance usually yields a somewhat higher percentage of silver. Strong ammonia appears to be without action on the yellow acetylide, and the quantity present during precipitation does not influence the composition of the precipitate.

Silver estimations in eight specimens dried over sulphuric acid gave percentages of silver ranging from 87·38 to 88·85. Of these two had been tried for three and six weeks respectively, and yielded 88·7 and 88·8. Blockmann's formula C_2Ag_2,H_2O requires 8·37; that of Berthelot, $C_2Ag_2,\frac{1}{2}H_2O$ or $(C_2HAg_2)_2O$, 86·7.

An attempt to prepare silver acetylide in neutral or acid solution, so as to diminish the risk of the precipitate carrying down with it silver oxide, was successful. Silver acetate is completely precipitated by acetylene with separation of the whole of the acetic acid. The acetylide so prepared has the same properties as that obtained in ammoniacal solution, but has not the same tendency to turn brownish on drying; and, like the latter, separates as a yellow, curdy precipitate, but may become white under the same conditions.

The silver was estimated in fifteen specimens carefully dried in a vacuum over sulphuric acid until they ceased to lose weight, and in some cases at 60—70°. The results lay between 86·6, the percentage of silver required for $C_2Ag_2,\frac{1}{2}H_2O$, and 87·9, nearly that required for—

$$C_2Ag_2{\cdot}\tfrac{1}{2}H_2O,\ 87{\cdot}8.$$

Drying at 60—70° caused a slight loss of weight, but caused the precipitates to darken. Those specimens which had become white yielded higher results than those which remained yellow. Two portions of the same precipitate, of which the one was left in contact with strong ammonia for several days, were dried, and yielded the same percentage of silver, 86·56.

The acetylene given off from a known weight of the dry substance with chlorhydric acid was measured and the silver chloride weighed; ratio of silver to acetylene, as 38 to 20 or 10·3 per cent carbon, $C_2Ag_2,\frac{1}{2}H_2O$, 9·7. Percentage of silver, 87·47. Other experiments by the same method, made with acetylide from ammoniacal silver nitrate and from silver acetate, also gave 1 mol. of acetylene to 2 atoms of silver.

Silver chloride dissolved in ammonia gave a yellow acetylide containing 87·85 per cent silver, and free from silver chloride.

Silver nitrate, in aqueous solution (decinormal), is precipitated by acetylene, three-fourths of the acid being liberated. Precipitates prepared from solutions of different strengths contained varying proportions of silver nitrate.

Alcoholic silver nitrate yields a precipitate much richer in nitrate, containing equal amounts of silver as acetylide and as nitrate. The action of hydrocarbons of the acetylene series on alcoholic silver nitrate has been studied by Behal. My analyses of precipitates from the nitrate gave as limits $3C_2Ag_2{\cdot}2AgNO_3Aq$ and $C_2Ag_2{\cdot}2AgNO_3Aq$, the latter being obtained from alcoholic solutions.

Silver sulphate solutions are also completely precipitated by acetylene, and with a solution containing 0·2 grm in 100 c.c. two-thirds of the sulphuric acid was set free. Precipitates obtained from such a solution give results corresponding to $2C_2Ag_2{\cdot}Ag_2SO_4Aq$.

II.—*Mercury Compounds.*

Mercuric acetate solutions yield white precipitates which become grey towards the end of the precipitation. If the solutions are not too strong the whole of the metal is thrown down with separation of all the acetic acid.

When washed with alcohol and dried *in vacuo* over sulphuric acid the substance has the composition required by the formula $3HgO2C_2H_2$. It resembles the compound $3HgO2C_3H_43HgCl_2$, obtained by Kutcheroff (*Ber.*, xvii., 13), from allylene, for, unlike the acetylides generally, it does not give off acetylene on treatment with chlorhydric acid, and is not explosive.

Iodine attacks it, apparently with formation of iodoform.

Mercurous acetate freshly precipitated and suspended in water is decomposed by acetylene and is converted into a greyish substance which differs entirely from the mercuric compound, and seems to be similar to silver acetylide in composition and properties. It detonates when heated suddenly, and gives acetylene on treatment with chlorhydric acid. Iodine acts upon it in the same way as upon silver acetylide, yielding di-iodacetylene.

The acetylene used was prepared from the copper compound obtained from the incomplete combustion of coal gas, and was purified by caustic soda.

I propose to continue the study of the mercurous compound and the action of iodine on this and other acetylides.

24. "*Isomerism amongst the Substituted Thioureas.*" By Augustus E. Dixon, M.D.

The author notes that, while it has been established that the addition product of a thiocarbimide XNCS with a primary amine YNH_2 is identical with that resulting from the combination of the thiocarbimide YNCS with the amine XNH_2, no investigation appears, as yet, to have been conducted with the object of determining whether identical or isomeric forms would result if the substituting groups are similarly transposed in thiocarbimide and secondary amine.

In a communication recently made to the Society (*C. S. Trans.*, 1891, 551), two isomeric forms of methylphenylbenzylthiourea were incidentally described, but it was left undecided whether two ethylphenylbenzyl compounds resulting from the action of ethylthiocarbimide on benzylaniline, and of benzylthiocarbimide on ethylaniline, respectively, were identical or isomeric. Their isomerism has since been established by the observation that when heated with alcoholic ammonia, under pressure, the former yields ethylthiourea and benzylaniline, the latter benzylthiourea and ethylaniline. Furthermore, a third isomer is now described, produced from phenylthiocarbimide and ethylbenzylamine; this occurs in vitreous prisms insoluble in cold water, freely soluble in hot alcohol, chloroform, benzene, and carbon disulphide, and melting at 94—95°.

An isomer of Gebhardt's (*Ber.*, xvii., 3037) dimethylphenylthiourea (m. p. 114°, from MeNCS and MeNHPh) was also obtained, by the interaction of PhNCS and Me_2NH. It forms long white prisms, melting, without decomposition, at 134—135°. It is moderately soluble in boiling water, very freely in hot alcohol, and when boiled with aniline yields dimethylamine and thiocarbanilide.

25. "*Note on Diastatic Action.*" By E. R. Moritz and T. A. Glendinning.

It has been observed by one of the authors that brewers' worts, as they issue from the mash tun, remain constant in respect to their starch transformation products when digested for two hours at the same temperature as that at which the conversion was conducted. The diastase in these solutions therefore exercises within such a period no action on the starch products contained in it; but if fresh starch be added, the residual diastase is found yet to possess considerable power of liqueifying and saccharifying starch, although its energy is distinctly inferior to that of the original malt. The authors describe a series of experiments made with the object of comparing the energy of the original with that of the residual diastase.

They consider that the results entitle them to form the following conclusions:—

The attainment of a resting stage in the transformation of starch by diastase by no means shows that the energy of the diastase is exhausted. The energy of the "residual" diastase is, in fact, very considerable, even under conditions adverse to its activity. It is somewhat weakened by increasing the amount of starch it has to convert, but it is weakened to a marked extent by subjecting it for some time to a temperature exceeding the optimum one for saccharification. When, however, it is not exposed for any length of time, whether previous to the first or to subsequent transformations, to a temperature exceeding the optimum, it appears capable, after transforming a considerable amount of starch, to transform further quantities to nearly the same point, when such further quantities are added successively and subsequent to the attainment of the resting stage in the preceding transformation.

PHYSICAL SOCIETY.

Ordinary Meeting, May 27th, 1892.

Mr. Walter Baily, M.A., Vice-President, in the Chair.

The following communication was read "*On the Present State of our Knowledge of the Connection between Ether and Matter: an Historical Summary*," by Prof. O. J. Lodge, F.R.S.

Referring to difficulties connected with the aberration of light, if the medium were supposed to be carried along by the earth in its orbit, Dr. Lodge described Boscovich's suggested experiment with a telescope filled with water, carried out by Klinkerfues, who was led to conclude that the "aberration constant" depended on the medium within the telescope, Klinkerfues' experiments were repeated by Sir G. B. Airy, but not confirmed. Astronomical observations were not necessary to determine the point at issue, for a fixed source near a collimator might be used with advantage. Hoek has examined the subject in this way with similar negative results. It might therefore be concluded that surveying operations are unaffected by terrestrial motion. This result, however, did not prove the existence or non-existence of an ether drift relative to the earth, for since the source and receiver move together any effect produced by such a drift would be compensated by aberration due to motion of the receiver.

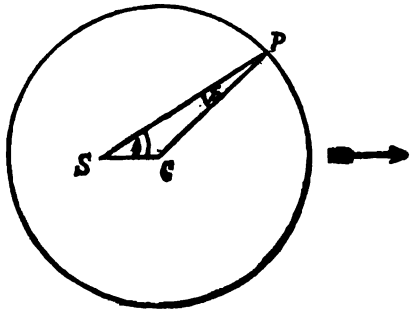
Speaking of refraction, he pointed out that if the ether were stationary in space, glass and other terrestrial bodies would have ether streaming through them, and that the refraction of say, glass, might differ as the direction of the ether drift through it varied. To test this Arago placed an achromatic prism over the object glass of a telescope on a mural circle, and observed the altitude of stars. To vary the direction of the ether drift through the prism, stars in different azimuths were observed, but the results showed no appreciable change in the deviation produced by the prism due to direction of the earth's motion. Maxwell used a spectroscope to test the same point. Light from illuminated cross wires passed through the telescope, prisms, and collimator, and was reflected back along the same path by a mirror and viewed through the telescope. Observations made with different aspects of instrument showed no change in the relative positions of the wires and their images.

Mascart had also tried the experiment with simpler apparatus, but was unable to detect any change.

These observations naturally suggest that the ether is at rest relative to the earth, but the apparently simple nature of aberration makes this view difficult to hold. Both phenomena are consistent with Fresnel's hypothesis, that only the excess of ether which the substance possesses over that of surrounding space moves with the body; for on this supposition the effects of altered refraction and ether drift compensate each other. Fresnel's view is practically established by Fizeau's well-known experiment on the effect of moving water on the velocity of light, and by the more accurate numerical results

obtained by Michelson. The only other theory which accounts for the experimental results is one by Prof. J. J. Thomson, which requires that the velocity of light in Fizeau's experiment should be altered by half the velocity of the medium. For media whose refractive indices are $\sqrt{2}$, the two theories lead to the same result, and as the indices of substances such as water do not differ much from this value, it is difficult to discriminate between them.

Looked at in another way Fizeau's experiment raises a difficulty; for, as Dr. LODGE pointed out, all water is moving with the earth, hence light should be hurried or hindered, according to the direction in which it passes through the water. This effect doubtless exists, but the results of it have never been detected by experiment. It is therefore necessary to inquire why the effect could not be observed directly, for the experiment had been tried with interference apparatus by Babinet, Hoek, Jamin, and Mascart, and in no case was any effect observed. It would therefore seem as if the ether must be stagnant, *i.e.*, stationary relative to the earth. Mascart had also tested whether Newton's rings or the rotatory power of quartz were affected by ether drift, but with negative results. These observations are, however, likewise compatible with Fresnel's hypothesis of an ether fixed relative to matter, and a free ether of space permeating all sub-



stances, for, according to this view, there is no more motion of the ether in water or glass than in air; hence the time of journey round a closed contour is independent of the direction in which the light traverses that contour. The time of journey between two points is also unaffected by terrestrial motion, as was proved by the experiments of Babinet, Hoek, and Mascart, on interference; hence he (Dr. LODGE) inferred that ether was either stagnant or had a velocity potential.

In moving ether it was necessary to define a ray, and Lorentz's method is the best. Suppose CP represents the velocity of light (V) in still ether, and SC the velocity of the ether (v), then a disturbance originating at S will travel along SP, which is the direction of the ray, whilst CP is the wave normal. In the above figure—

$$\frac{\sin\varepsilon}{\sin\theta} = \frac{SC}{CP} = \frac{v}{V} = a,$$

the constant of aberration. The velocity along the path of the ray is SP. Calling this velocity V′ we have, $V' = V\cos\varepsilon + v\cos\theta$. The path of a ray is determined by the time of journey being a minimum, and the formula—

$$T = \int_A^B \frac{ds}{V} = \text{a minimum},$$

is the equation to a ray, where A and B are the extremities, and ds an element of the path.

If the ether be moving, V′ must be substituted for V, and we get—

$$T' = \int_A^B \frac{ds}{V\cos\varepsilon + v\cos\theta} = \text{a minimum}.$$

This integral can be written exactly—

$$T' = \int \frac{ds}{V}\,\frac{\cos\theta}{1-a^2} - \int \frac{v\cos\theta}{V^2(1-a^2)}\,ds =$$

$$= \frac{T\cos\beta}{1-a^2} - \int \frac{v}{V^2}\,\frac{\cos\beta}{1-a^2}\,ds.$$

The last term is the only one involving the first power of ether drift, and it vanishes in case there is a velocity potential; for since $v\cos\theta = \frac{d\phi}{ds}$, where ϕ is the velocity potential, it may be written $\frac{\phi_B - \phi_A}{V^2(1-a^2)}$, and so its value depends only on the end points, and not on the path. If these points are the same, *i.e.*, the contour is closed, it becomes zero, and reconciles all the experiments hitherto made. It must be admitted, however, that if a is not a constant the question is again opened, but there is no reason to suppose it can vary in the same horizontal plane.

If the medium be changed, V becomes $\frac{V}{\mu}$, and in order to retain the same velocity potential in the changed medium, v must become $\frac{v}{\mu^2}$, which is Fresnel's law. Hence Prof. LODGE pointed out that the velocity potential condition includes Fresnel's law as a special case.

It can, in general, be inferred that *no first order optical effect due to terrestrial motion can exist in a detectable form.* It is always compensated by something else. Quantities of the second order of magnitude must therefore be attended to. From the first equation above, it follows that $\cos\varepsilon = \sqrt{1-a^2\sin^2\theta}$, and the time of journey in moving ether is given by—

$$T' = T\,\frac{\sqrt{1-a^2\sin^2\theta}}{1-a^2},$$

where T is the time if everything were stationary. This is, in brief, the theory of Michelson's recent experiment. If the light travels along the ether drift $\theta = 0$, and

$$T' = \frac{T}{1-a^2},$$

whilst if $\theta = 90°$,—

$$T' = \frac{T}{\sqrt{1-a^2}}.$$

Therefore the velocity along the ether drift should differ from that across the drift in the ratio of $\sqrt{1-a^2} : 1$. This point has been very carefully tested by Michelson, but nothing approaching to a quarter of the theoretical effect was observed. His negative result would seem to preclude any relative motion, even irrotational, and show that the ether is at rest relative to the earth's surface. On the other hand, the author (Dr. LODGE), has recently made experiments on the influence of rapidly rotating steel discs on the ether, which prove that the ether is not affected by the motion of contiguous matter to the extent of a 200th part of the velocity of the matter. These experiments are at present in conflict. Prof. Fitzgerald has suggested a way out of the difficulty by supposing the size of bodies to be a function of their velocity through the ether.

Returning to the statements which have been made of Fresnel's law, Glazebrook has shown that actual extra density of ether is not necessary, for if the virtual mass be altered, the same results follow; all that is required is a term depending on the relative acceleration of ether and matter. To modern ideas the loading of the ether by the presence of matter is most likely to be correct, and the observed effects of relative motion are regarded as the results of secondary reactions of matter on ether. On this

view the ether of space may be wholly unaffected by the motion of matter. On the vortex ring theory of matter, it is not unnatural to suppose that the ether in its neighbourhood should be only affected irrotationally by its motion. And if the velocity potential be granted, nothing of the nature of viscosity being admissible, the results of all the interference, refraction, and aberration experiments could be predicted, and the whole theory is as simple as it can possibly be. The only reliable experiment ever made which tends against this view is that of Michelson. The author surmised that this must somehow be explained away.

In reply to a question by Prof. Ayrton, Dr. Lodge said that when air was substituted for water in Fizeau's experiment, no effect is observed. This might have been expected, for the difference in the times of journey by the two paths depended on $\frac{\mu^2-1}{\mu^2}$, and as μ is nearly unity for air, the air effect is too small to see.

(Note by Dr. O. J. Lodge.—In Hoek's interference experiment it might be said that ether moving in stationary water is balanced by that of the ether moving in stationary air; but while motion of water itself would disturb the balance, motion of air would do nothing appreciable. The only kind of motion that could display an optical effect is rotational motion, or motion of layers at different speeds, not a simple uniform drift.

Prof. J. V. Jones asked how the Fizeau experiment could be expressed on the loaded ether theory; for since the speed of matter affects the velocity of light, it seemed to involve a directional loading. A mere extra density term or acceleration coefficient will not explain this; it seems to require a coefficient of a velocity term. This question has been hinted at by Lord Rayleigh, who points out (under the heading "Aberration," *Nature*, March, 1892) that the rate of propagation of waves on a loaded string will be affected by a travelling of its load. The question is not perfectly simple, and the analogy not complete. A good deal depends on the nature of the connection symbolised as "loading)."

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY IN COURT.

To the Editor of the Chemical News.

Sir,—The Institute of Chemistry, a body which is endowed with a charter, has at length exercised its disciplinary powers and expelled one of its Fellows. But whilst maintaining its technical right to expel for unprofessional conduct, or for what it deems to be unprofessional conduct, it has in this instance awarded to its expelled Fellow a valuable testimonial in the shape of a declaration in the Queen's Bench Division of the High Court, that the expulsion "casts no imputation upon the professional capacity or personal character" of the expelled Fellow.

This seems very strange. We can easily understand that a Fellowship lapsing through inability or unwillingness to pay the annual subscription requisite to keep up the Fellowship, should not cast any imputation on the holder of the Fellowship. But that a deliberate expulsion from the Institute,—and an expulsion following upon a refusal to resign,—should cast no imputation, that is wonderful indeed.

The explanation is, however, supplied by the record of the proceedings in the case.

The cause of the expulsion was in this instance of a political character. The expelled Fellow, who had an objection to the assumption of the functions of Public Analyst by an alien, gave effect to his objection by making an application for an appointment of Public Analyst where there was an alien analyst.

Thereupon two events happened. The alien analyst took out letters of naturalisation and complied with the law, and at the same time complained to the Institute, which expelled its Fellow whose public spirited action had put a stop to a grievous scandal.

Hence the strange anomaly of expulsion from the Institute of Chemistry being accompanied by the bestowal of a valuable certificate of character and competence.

The Institute possesses arbitrary powers. Any one of its Fellows is liable to expulsion upon the most frivolous of pretences; but a frivolous expulsion brings in its train a certificate of character and competence which is at least as valuable as the Fellowship, and is certainly a more permanent possession.—I am, &c.,

J. Alfred Wanklyn.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxiv., No. 22, May 30, 1892.

On Cadmium Hydrosilicate.—G. Rousseau and G. Tite.—The hydrosilicate, $2(CdO,SiO_2).3H_2O$, is soluble in hydrochloric acid, with deposition of pulverulent silica. It loses little of its water at dull redness. Near orange redness it melts to a colourless transparent glass, and undergoes a loss of weight greater than that due to its total dehydration.

On Strontium Phosphate.—L. Barthe.—The author describes the neutral compound, PO_53SrO, the monacid compound, $PO_52SrOHO$, and the diacid compound, $PO_5SrO,2HO+2HO$.

The Calorific Power of Coal, and Formulæ for its Determination.—M. Scheurer-Kestner.—This paper does not admit of useful abstraction.

Mechanical Determination of the Boiling-Points with Complex Terminal Substitution.—G. Hinrichs.—A purely mathematical paper.

Certain Reactions of the Three Amidobenzoic Acids.—Oechsner de Koninck.—If orthoamidobenzoic acid is heated with a small excess of pure potassium nitrite there is formed a colouring-matter which dissolves with a garnet-red colour in water containing a little alcohol. If meta- and para-amidobenzoic acids are similarly treated they form red colouring-matters soluble in dilute alcohol. If we treat the acids with a small excess of pure ammonium nitrate and heat gradually to fusion we see two strata, the lower light red and the upper violet. With a smaller proportion of the salt there is formed a dark red or brown colouration. If we allow the mixture to cool for a moment and then add a little water, the liquid is decolourised. On heating again it resumes its original colour. If we heat gently mixtures of uranium nitrate and of the three isomers, we find with the ortho-acid the formation of a bright red sublimate, whilst alcoholised water takes an amber yellow. With the meta-acid the sublimate is brown, and the alcoholic water takes a red-brown colour. With the para-acid the sublimate is orange, and the solution in alcoholic water is deep yellow. Chloride of lime was used as a paste. On mixing equal portions of this and of the ortho-acid there was formed a deep violet paste. When cold it was taken up in concentrated acid, giving a solution bright red by transmitted light, but reddish-brown by reflection. After some time there appeared a fine violet fluorescence. With the meta-acid the liquid was a solferino-red by transmitted, but bright red by reflected light; no fluorescence. The para-acid gave a deep red alcoholic solution not fluorescent. Mixtures were made up of equal parts

of granulated zinc chloride and the three isomers, and heated to the melting point of the latter. The ortho-acid gave an amber colour and dissolved in hot concentrated alcohol. The meta- and para-acids yielded a deep violet colour. Sometimes greenish reflections were observed. With stannous chloride heated progressively the mixture of ortho-acid and of a slight excess of the salt melted to a thick amber liquid. The meta-acid gave a yellowish white liquid, and the para-acid a bright yellow. Water and alcohol dissolved nothing in the cold. The ortho-acid, if heated gently with a slight excess of stannic chloride and allowed to cool, dissolved in alcoholised water with a solferino-red. The meta- and para-isomers gave no reaction.

The Composition of Chlorocruorine.—Dr. A. B. Griffiths.—This substance is a respiratory pigment, existing in two states, oxidised and reduced. The former presents two absorption bands, the one between C and D and the other between D and E. The reduced chlorocruorine has only one band between C and D, less definite. The author has determined the composition of this pigment as obtained from the blood of *Sabella*. The result leads to the complex formula $C_{560}H_{845}N_{143}FeS_3O_{167}$. According to Prof. Church, turacine, from the feathers of the turaco, is represented by the formula—

$$C_{82}H_{84}Cu_2N_9O_{32},$$

and presents some analogies with hæmatine.

The Antiseptic Properties of Formaldehyd.—A. Trillat.—One of the most remarkable properties of formic aldehyd is its sterilising property. Urine mixed with this liquid becomes incapable of putrefaction. Its sterilising power with broth containing *Bacillus anthracis* is still more marked than that of mercuric chloride.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Cyanides.—Can any of the readers of the CHEM. NEWS inform enquirer where Dr. Kennblanch's method for the estimation of cyanides in spent oxide from gas-works can be found?—J. P.

Analytical Chemists as Jurymen.—Could any of the readers of the CHEMICAL NEWS inform me whether analytical chemists can claim exemption from serving as jurymen (common) at Assizes and Quarter Sessions, on the ground that they are professional men?—ANALYST.

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Photographic, 8.
WEDNESDAY, 22nd.—Geological, 8.
THURSDAY, 23rd.—Royal Society Club, 6.30. (Anniversary).
FRIDAY, 24th.—Physical, 5. "Breath Figures," by W. B. Croft. "The Measurement of the Internal Resistance of Cells," by E. Wythe Smith. "Units of Measurement," by Mr. Williams.

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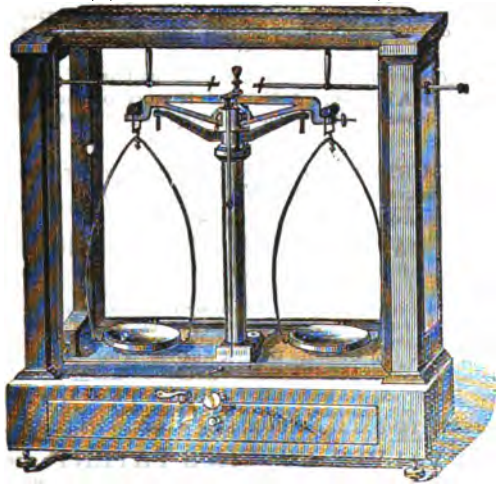

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of STRONTIA, BARYTA, &c.

CARAMELS for all purposes.

A. BOAKE, ROBERTS, & CO.
STRATFORD, LONDON, E.

THE CHEMICAL NEWS.

VOL. LXV., No. 1700.

THE FLAME OF BURNING NITROGEN.

By W. CROOKES, F.R.S.

NITROGEN is a combustible gas; that is to say, a mixture of nitrogen and oxygen (atmospheric air) will under certain conditions burn with a flame, and production of nitrous and nitric acids. The reason why, when once nitrogen is set on fire, the flame does not spread throughout the whole atmosphere and deluge the world in a sea of nitric acid, is that the igniting-point of nitrogen is higher than the temperature produced by its combustion, and therefore the flame is not hot enough to set fire to the adjacent gas.

In the experiments shown at the Soirée of the Royal Society on June 15th, an electric current of 65 volts. and 15 ampéres, alternating 130 times a second, was passed through the primary of a large induction coil, when an arching flame, consisting chiefly of burning nitrogen, issued from each of the secondary poles, meeting at the centre. When once started the poles can be drawn asunder till the flame bridges across 212 m.m. When the teminals are more than 46 m.m. apart, the flame will not strike across. When alight the flame is easily blown out by the breath, and it can then be re-lighted by a taper.

In the spectroscope the flame of nitrogen shows no lines, the spectrum being faint and continuous. The temperature is a little higher than that of a good blowpipe flame, easily melting fine platinum wire. The hot gases rising from a flame have a strong odour of nitrous acid, and when it is produced in a closed globe, the interior rapidly fills with red gases.

The flame produced by exciting an induction coil by means of an alternating current was first observed by Mr. Spottiswoode, F.R.S., who described it before the Royal Society in 1880. It has lately been exhibited on a magnificent scale at the Crystal Palace, by Messrs. Siemens Bros., and by Messrs. Swinburne and Co. It is not known, however, that any chemical explanation of the flame has before now been published.

NOTE ON THE ANALYSIS OF SLAG OF METALLIC APPEARANCE FROM THE MANUFACTURE OF PHOSPHORUS IN ELECTRICAL FURNACES.

By JOHN C. CHORLEY, F.C.S.,
University College, London.

THE process of manufacture in which this slag is formed may be briefly described as follows:—The materials, consisting of redonda phosphate (native phosphate of alumina), some form of calcium phosphate, carbon, and sand, are first heated in an auxiliary furnace and are then fed into the electrical furnace, built of firebrick, in the form of a rectangular trough. An alternating current of about 5000 ampères with an E.M.F. of 50—60 volts. is employed (*Journ. Soc. Chem. Ind.*, x., 5445). Owing to the intense local heat, most of the oxygen combines with the carbon present and phosphorus distils over. Two distinct kinds of slag are formed, that largest in quantity being chiefly silicate of lime and alumina, whilst the other, containing iron, silicon, and phosphorus, is distributed throughout the mass in more or less globular buttons. Three separate samples of this latter slag were obtained at different tappings; all were steel-grey in colour, very hard and brittle, and breaking with a metallic fracture; it appeared quite homogeneous, but did not exhibit any crystalline form under the microscope. When examined in the state of very fine powder with a $\frac{1}{4}$th objective, a few particles of transparent matter were observed, evidently silica. The slag is extremely stable; it is easily fusible with the oxyhydrogen blowpipe, a little oxidation taking place. Hydrochloric and nitric acids, dilute or concentrated at 100°, have little or no action upon it. After being heated to 100° with aqua regia for thirty hours very little action could be detected. With hydrofluoric acid it is practically unaltered.

With dilute sulphuric acid a similar result was obtained; but long boiling with concentrated sulphuric acid decomposes it partially.

Direct fusion in a platinum crucible is impossible, as the phosphorus at once attacks the platinum.

When heated in a current of sulphuretted hydrogen a superficial layer of sulphide of iron is formed.

There is very little action when it is heated with bromine or iodine.

Only two methods of decomposition were found available for analysis.

1. By heating the finely-powdered slag in a porcelain boat in a current of dry chlorine, and passing the gases first through water and then through a dry plug of cotton wool to retain solid particles, the iron was then volatilised as Fe_2Cl_6, the silicon as $SiCl_4$, which was decomposed by the wash water, and the phosphorus as PCl_5 or PCl_3; in about an hour complete decomposition was effected, only a little silica being left in the boat. The contents of the whole apparatus were then washed into a basin, and after the addition of hydrochloric acid evaporated to dryness and heated to render silica insoluble.

After adding weak hydrochloric acid the silica was filtered off and weighed; the filtrate was then evaporated several times to dryness with nitric acid in order to oxidise the phosphorus completely, and was finally dissolved in weak hydrochloric acid and diluted to 250 c.c. The iron in 25 c.c. was estimated by titration in sulphuric acid solution with permanganate of potash, and the phosphorus in 25 c.c. as $Mg_2P_2O_7$, with intermediate precipitation with ammonium nitro-molybdate, and in certain cases directly as ammonium phospho molybdate.

2. This method, in part new, was as follows:—(*a*) The finely-powdered slag was heated with excess of a neutral solution of copper sulphate in a sealed tube to about 170° for four to five hours. A considerable quantity of metallic copper was precipitated with some phosphide of copper, while some iron, phosphorus, and silicon went into solution; when the tube was opened there was no pressure. The contents were washed out and treated with sufficient nitric acid to dissolve the copper, and the residue was filtered off; the filtrate was then evaporated to dryness with hydrochloric acid and silica estimated. The copper in the filtrate was precipitated with hydrogen sulphide and the filtrate from this added to the similar filtrate in the second part of this method. (*b*) The residue from (*a*) was fused with about five times its weight of fusion mixture at a bright red heat for one hour in a platinum crucible, and when cold the contents were dissolved in dilute hydrochloric acid and evaporated to dryness, and silica estimated as usual. The filtrate was then mixed with the filtrate from (*a*) made up to 250 c.c., and the analysis was continued as in the first method.

The mean results obtained were as under:—

	Sample No. 1.	Sample No. 2.	Calculated for Fe_4PSi_2.	Sample No. 3.	Calculated for Fe_2PSi.
Fe	70·55	68·75	72·02	73·79	74·01
P	9·84	10·84	9·97	14·63	13·63
Si	17·90	19·10	18·00	10·31	12·33
O and loss ..	1·71	1·31	—	1·87	—

This slag may be a definite compound containing a small amount of impurity. The analysis of Nos. 1 and 2

agrees fairly well with the formula Fe_4PSi_2, and that of No. 3 with Fe_3PSi. Or it may be a mixture of silicide and phosphide of iron in varying proportions. As it is not crystalline, the last view is perhaps the correct one; yet silicide of iron is easily attacked by acids, and this compound is not, and its power of resistance may be due to the existence of some definite compound.

The specific heat was determined and found to be 0·146, being very close to that calculated for a mixture of its constituents, viz., 0·142, the specific heat of iron being taken as 0·114, that of phosphorus as 0·174, and silicon as 0·173 (Regnault). The specific gravity was found to be 5·965. The substance is a conductor of electricity.

MOLYBDIC ACID AS A COLOUR REAGENT FOR CERTAIN AROMATIC OXY-COMPOUNDS.

By J. STAHL.

HAGER some time ago indicated a reaction for the tannic acid of galls and other tannic acids, according to which these substances give fine reddish-yellow colours with ammonium molybdate. I have found that the same reactions occur for certain compounds approximating on tannin, pyrogallol, pyrogallo-carbonic acid, and gallic acid. As all four substances named contain oxy-groups in an ortho-position to each other, the reagent was tried also for other aromatic compounds in which the same case occurs. The result was that ammonium molybdate is a specific colour-reagent for all aromatic compounds which contain two or more oxy-groups standing in the ortho-position to each other.

Ammonium molybdate produces intense phenomena of colouration only with such bodies, which, according to the substance employed, may be yellow, reddish-brown, or blackish-brown. On the contrary, in all organic compounds in which the above mentioned condition does not occur no colouration is recognised. Thus, with pyrocatechin on the addition of the molybdate there is shown an intense reddish brown colour, which does not appear with hydroquinone and resorcine,—a behaviour which shows phloroglucine in contrast to pyrogallol. The following aromatic compounds display similar colourations:—Protocatechuic acid, caffeic and hydrocaffeïc acid, phenanthrenehydroquinone and retenehydroquinone; in alizarin, purpurin, anthragallol, and rufigallic acid, the aqueous solutions of which are yellow or red, the tone is much intensified by an addition of the molybdate. The entrance of other groups into the nucleus does not generally interfere; thus the reaction appears in the bromo- and nitro-derivatives of pyrogallol and gallic acid, but not in the phenol ethers, where one or more hydrogen atoms of the oxy-group are replaced by alkyles, as guaiacol and vanilline. Very slight yellow colourations which may occur with the two last mentioned bodies are probably due to slight impurities. Among compounds of a less fully known constitution the reaction is produced by quercitrin and its scission product quercetin, apomorphin, podophyllin, koussein, and aloin.

The aqueous solution of free molybdic acid behaves exactly like ammonium molybdate. The latter, in presence of organic substances, passes to a lower stage of oxidation, with the production of a blue, yellow, or a reddish-brown.

The origin of the colour phenomena in question depends on the oxidising action of molybdic acid and its ammonium salt. As those aromatic compounds which contain oxy-groups in the ortho-position to each other are more unstable and especially more readily oxidisable than their isomers, there occurs here a more energetic reduction of the molybdic compounds. The stage of the blue oxide is overleaped, and there appear at once the lower brownish stages of oxidation. If heat is applied and the reaction is prolonged, brownish-black masses separate out which are found to be a variable mixture of lower molybdic acids, whilst a portion of the organic substance is oxidised to carbonic acid and water. But it is not impossible that there may appear simultaneously yellow or brown oxidation products of the oxy-compounds.

The sensitiveness of these reactions is not very great, but in case of pyrocatechin, pyrogallol, gallic acid, and tannin, it admits of the recognition of 0·1 m.grm. substance in 1 c.c. of liquid. The action of sodium tungstate is similar to that of ammonium molybdate.—*Ber. Deuts. Chem. Gesell.*

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 293).

IF the loss of weight during this decomposition could be compared with the deficiency of sulphuric acid in the residue, it is evident that an indirect means would be at hand for the detection of a possible simultaneous loss of water. Such a circuitous road seemed to be the only one open to the present search.

In the series of experiments tabulated below, pure cupric sulphate was heated in the usual manner to 250°, and then after the addition of sulphuric acid to 400°, until the salt became constant in weight. The heat was then increased to dull redness, and after cooling the loss of weight was determined. Upon solution of the residue in water a small amount of basic salt was naturally deposited. Since the filtrate was apparently quite normal, it is evident that the amount of sulphuric acid necessary exactly to dissolve this precipitate must have been equivalent to the anhydride driven off.

After standing a considerable time, the basic salt was carefully filtered off and a measured amount of twentieth normal acid was used for its solution. The crucible used for the ignition was also washed with a measured quantity of acid. The clear solutions were all combined, and the excess of acid was determined by sodic hydroxide and methyl orange. Since the loss of weight upon ignition was noticeably more than the amount of anhydride corresponding to the quantity of sulphuric acid used to dissolve the basic salt, something beside sulphur trioxide must have been expelled by the heat.

The last column of the table gives the difference between the loss of weight of the cupric sulphate and the amount of sulphuric anhydride required to dissolve the basic salt, expressed in percentage of the original crystallised compound. This difference probably represents a small amount of water held even at 400°. The results showed a very noticeable variation, and at first sight appeared somewhat unsatisfactory. The first two experiments agreed well with each other, and were apparently very trustworthy. In the third, on the other hand, the amount of basic salt was so large as greatly to interfere with the accuracy of the result. In Experiment 23 the loss of weight upon ignition was so very large, amounting to about three per cent of the anhydrous sulphate, that the experiment was rejected. After such a failure it was natural that the next sample should not have been heated enough. This result is hence probably too low. The last experiment was more carefully regulated, and is more trustworthy. In this case the cupric sulphate was heated for an hour at very dull redness.

The filtrates from the precipitates of basic salt did not deposit any further solid upon long standing. That from the last determination was rendered very distinctly acid

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Action of Heat upon Cupric Sulphate.

Weights reduced to vacuum.

Number of Expt.	Weight of $CuSO_4.5H_2O$.	Weight of $CuSO_4$ [260°].	Weight of $CuSO_4$ [400°].	Weight after ignition at dull redness.	Loss between 400° and redness.	1·20 normal H_2SO_4 required for basic salt. Uncorr.	Corr.*	Per cent of $CuSO_4.5H_2O$ unaccounted for.
	Grms.	Grms.	Grms.	Grms.	M.grms.	C.c.	C.c.	
20.	—	1·5822	1·57945	1·57325	6·2	2·65	2·55*	0·044
21.	2·71828	1·7413	1·73836	1·73130	7·06	2·95	2·85*	0·050
22.	4·7325	—	3·0258	2·9928	33·0	16·36	[15·86*?]	[0·030?]
23.	2·01084	1·2880	1·2856	1·2504	35·2	—	—	—
24.	7·211	—	4·6075	4·6055	2·0	0·33	0·32*	0·019
25.	3·979	—	2·5443	2·5403	4·0	0·93	0·90*	0·055
						Total average		0·040
						Average omitting 22..		0·042

(* See Experiments 26—27).

to methyl orange by the addition of a milligrm. of sulphuric acid, in spite of the difficulty in detecting the colour-change in the presence of the blue cupric sulphate. These tests indicate that the filtrate was wholly normal.

In order to test still more definitely the accuracy of the method the following mode of procedure was devised. To neutral solutions of cupric sulphate—prepared either from the purest crystals or by long standing after the neutralisation of the trace of acid in ordinary "chemically pure" material—were added small measured amounts of a standard sodic hydroxide solution. After a time the precipitate was filtered off and dissolved in standard sulphuric acid, exactly as if it had been obtained by the expulsion of the acid through heat.

Test of Method.—Precipitation and Solution of Basic Cupric Sulphate.

No. of experiment.	Concentration of solution.	Time between precipitation and filtration.	Twentieth normal NaOH used.	Twentieth normal H_2SO_4 used.	Factor $\frac{\text{c.c. NaOH}}{\text{c.c. } H_2SO_4}$
			C.c.	C.c.	
26.	Strong.	10 mins.	3·00	2·85	1·05
27.	Strong.	90 mins.	3·00	2·94	1·02
28.	Medium.	15 hours.	3·00	3·14	0·95
29.	Dilute.	1 hour.	6·00	6·24	0·96
30.	„	90 mins.	6·00	6·27	0·95
31.	„	„	3·00	3·12	0·96
32.	„	„	3·00	3·14	0·95
33.	„	„	3·00	3·03	0·99
		Average of Experiments 28-33			0·96

It is hence evident that from dilute solutions the basic salt is wholly precipitated in a comparatively short time. Even under the worst conditions no deficiency approaching that noticed in Experiment 25 was observed. Another series (Experiments 34—37), made in very dilute solutions without filtering, gave values for the factor which respectively equalled 0·97, 0·98, 0·95, and 0·98. The average is 0·97, not seriously different from that found above. The first value of the factor was used in correcting the results of Experiments 20—25. The correction involved is extremely slight except in Experiment 22, where the application of the full value of the factor to a very large quantity is of doubtful advisability. Hence it is better to omit this experiment from the final average.

One contingency alone is not provided for by these test experiments; that is to say, the formation of a cuprous compound and its solution in the cupric salt. The formation of a cuprous salt by gentle ignition of cupric sulphate in the air is far from probable; but for fear that such a reaction had taken place, the solution of the cupric sulphate was usually exposed to the air from twelve to twenty-four hours before filtration. The fact that exposure to the air for a long time after filtration caused no further formation of precipitate is a satisfactory proof that no cuprous salt remained in solution, even if it had been formed in the first place.

The outcome of all these more or less indirect experiments points to the conclusion that cupric sulphate retains about 0·12 per cent of its water of crystallisation, even when heated to 400° C. This last trace of water is given off only at a temperature at which the cupric sulphate itself begins to decompose. It must be admitted that the evidence upon the point is not absolutely certain, but there is no doubt of its great probability. Upon such a matter as this it is difficult to see how more definite results could have been procured.

Total Percentage Composition of $CuSO_4.5H_2O$.

	Per cent.
Water lost at 360—400°	= 36·067
„ „ between 400° and redness	= 0·042
Copper, average	= 25·449
SO_4	= 38·436
Total	= 99·994

If the amounts of copper and sulphuric acid supposed to be lost during the electrolysis are added, the total becomes 100·004.

Either of these total results is now accurate within the limits of error of ordinary analysis. But it will be seen that the total percentage of crystal water indicated by the analysis is much too large as compared with the sulphuric acid, which is our only certain standard of reference. This excess of water must have been occluded in the original crystals, which were not very finely powdered. Accordingly two specimens of the purest cupric sulphate were much more finely pulverised, and their loss of weight at 400° was then found to be 36·057 (average of Experiments 21 and 23) instead of 36·067 per cent. Mr. H. M. Richards kindly measured many diameters in the two powders, and found that the particles of the coarser powder approximated one-tenth of a millimetre, while those of the finer were less than one-hundredth. Since more than half an hour's continuous powdering, at the very slow rate adopted to prevent warmth from friction, had been necessary to reduce a small amount of material to the finer state, it was concluded to abandon the attempt at obtaining cupric sulphate free from occluded water.

It must be remembered that the salt had been very slowly crystallised by the evaporation of the solution, and of course had had every opportunity to imprison traces of the mother liquor. Crystallisation from hot solutions could not be adopted because of the risk of the formation of basic salt (Hampe, *loc. cit.*). But even if the true amount of the water of crystallisation could have been determined, it would have been of little present use for the determination of the atomic weight of copper, because of the uncertainty of its molecular weight. It is hoped that an investigation of the quantitative relations of water in other compounds may be in progress during the coming year at this laboratory.

(To be continued.)

REDUCING AGENTS OF THE AROMATIC SERIES WHICH ARE CAPABLE OF DEVELOPING THE LATENT PHOTOGRAPHIC IMAGE.

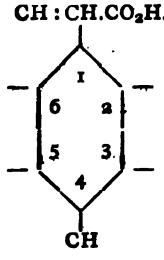
By A. and L. LUMIERE.

Authors have endeavoured to apply to photography the conquests of chemistry and to find a chemical theory for developers: from their observations the following conclusions have been drawn.

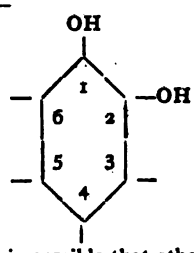
1. For a substance of the aromatic order to be a developer of the latent image there must be in the benzinic nucleus at least two groupings of hydroxyl or two of amidogen, or at the same time a hydroxylic and an amidogenic group.

2. The preceding condition is necessary, but it only seems sufficient in isomerism.

For example, orcine will not devel pe; its isomeride, toluquinone, developes perfectly. Resorcine indicated as developer has no action in the state of purity. Caffeic acid, however,—



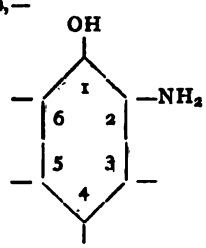
and pyrocatechin,—



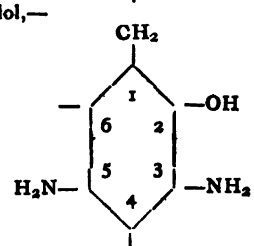
are developers. It is possible that other substances than the isomerides have reductive qualities, but these exist in all cases of isomeric relation.

3. The developing power may persist when in the molecule there are a greater number of groupings OH or NH_2.

Pyrogallic acid was already known; we may also mention diamidophenol,—



diamidocresylol,—



a triamidocresylol; gallamic acid.

4. When the molecule results from the welding of two or several benzinic nuclei, or of benzinic nuclei and others, the preceding remarks are only applicable when the hydroxylic groups and the amidogenic exist in the same aromatic nucleus.

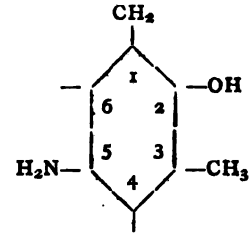
For example, benzidine has no action nor oxycarbostyryles, whereas paradioxyquinoleine acts.

5. The substitutions made in the group OH or the group NH_2 destroy the developing properties whenever at least two of these groups do not remain intact in the molecule.

For example, dimethylparamidophenol does not develope, neither does dimethylhydroquinone. Guaicol, however acts.

6. The other substitutions which may be made in the CH of the nucleus do not seem to suppress the developing power.

For example, hydrophlorone—



Podocarpic acid does not seem to annul the developing power. But the acid function seems to diminish it, for caffeic, protocatechuic, and amidosalicylic only develope with a strong base, the alkaline carbonates being no longer sufficient.

7. The preceding remarks only apply to the aromatic series.

Ethylendiamine and guanidine have no action. Phenylhydrazine is an exception, but, on the other hand, this compound is quite outside of the previous rules by its mode of formation.

The followine conditions must be added to the above. The substance must be soluble in water, its solution little coloured, and the products of its oxidation in the bath must have little colour and not dye gelatin.

In a note in the June number of the *Bull. de la Soc. Française de Photographie* the authors indicate the following formulæ for the application of paramidophenol to the development of gelatino-bromide of silver.

I.

Water	1000
Sulphite of soda	200
Carbonate of soda	100
Paramidophenol	12

II.

Water	1000
Sulphite of soda	200
Carbonate of lithia	12
Paramidophenol	12

The first formula is very energetic and is particularly suitable for instantaneous developments.

The slight solubility of paramidophenol does not give the latitude in the formulæ which pyrogallic acid presents, for example. But, per contra, the solution is preserved for a long time colourless and active.

Finally, in a recent communication to the French Photographic Society Messrs. Lumière publish a comparative study on hydroquinone, paramidophenol, and ikonogene. Leaving aqueous solutions of these three compounds in the air the paramidophenol oxidates first, then ikonogene; hydroquinone resists longest.

The product from oxidation of the paramidophenol, probably quinonimide, is insoluble in water; the solution is not disturbed, but deposits a black soluble precipitate,

which turns violet in ammonia or alkali and red in nitric acid.

With ikonogene the solution is coloured deep brown, turning green in ammonia and red in nitric acid.

Finally, the oxidated solution of hydroquinone is reddish, becomes yellow in ammonia, and is discoloured by nitric acid.

These same products form in developing; those of ikonogene and hydroquinone dye gelatin yellow, which remains colourless in the case of paramidophenol. At least 25 clichés can be developed with this last substance without finding any difference from first to last; whereas with the two others as soon as some clichés have been developed the others turn yellow.

These three compounds reduce soluble salts of silver, but have no action on haloid salts except in presence of an alkali or alkaline carbonate.

The addition to the developer with paramidophenol base of bromide of potassium or hyposulphite of soda produces almost similar effects as with the other developers.

By the Reeb process, to fix the weight of necessary matter to reduce 1 grm. of nitrate of silver, the authors obtained the following numbers:—

Hydroquinone	0·07
Paramidophenol	0·14
Ikonogene	0·30

It then requires twice as much paramidophenol and four times as much of ikonogene to reduce the same weight of nitrate of silver. From a practical point of view these differences are of no importance, for the reducing agent is always in great excess as regards the salt of silver. Paramidophenol, however, seems to present these advantages. It oxidates more rapidly, and in consequence is more energetic and developes more rapidly. The products of its oxidation have no injurious effect on the image or gelatin.

The best proportions are, it seems, as follows:—

Water	500
Carbonate of potash	40
Sulphite of soda	100
Paramidophenol	8

—*Moniteur Scientifique*, Jan., 1892.

METHODS FOR MILK ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

Water.

EVAPORATE 1 to 2 grms. of milk in a tared flat dish containing from 15 to 20 grms. of pure dry sand, or without sand, until apparently dry. Transfer to air bath and dry for one hour at temperature of boiling water. Cool in desiccator and weigh rapidly to avoid absorption of hygroscopic moisture.

Total Nitrogenous Matter.

Place in a Kjeldahl digestion flask a known weight (about 5 grms.) of milk and proceed exactly as described for this method by the nitrogen reporter.

Fat; Method of Adams, Modified by Wiley.

Coils made of thick filter paper, cut into strips 2·5 by 25 inches, are thoroughly extracted with ether and alcohol or the weight of the extract corrected by a constant obtained for the paper. About 5 c.c. of the well mixed milk are placed in a small beaker, covered with a watch glass, and weighed. From a weighing bottle about 5 grms. of milk are transferred to the coil by a pipette, care being taken to keep the end of the coil held in the fingers dry. The coil, dry end down, on a piece of glass is dried at the temperature of boiling water for one hour, or better dried in hydrogen at temperature of boiling water, transferred to a syphon extraction apparatus, and extracted by at least 12 syphonings with absolute ether or petroleum spirit boiling at about 45° C. The extracted fat is dried in hydrogen and weighed.

Alternate Method of Estimating Water and Fat in Milk.

Method of Babcock.—In the bottom of a perforated test tube is placed a clump of clean cotton; the tube is then filled three-quartera full of ignited asbestos, lightly packed, and a plug of cotton inserted over it. The tube and contents are weighed and the plug of cotton carefully removed and 5 grms. of milk from a weighed pipette run into it, and the plug of cotton replaced. The tube, connected at its lower end by a rubber tube and adapter with a filter pump, is placed in a drying oven at a temperature of 100° C., and a slow current of dry air drawn through it until the water is completely expelled, which in no case requires more than two hours.

The tube containing the solids from the above operation is placed in an extraction apparatus and exhausted with ether in the usual way.

The Estimation of Sugar.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:—

Reagents.—1. *Basic plumbic acetate*, specific gravity 1·97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid mercuric nitrate.* Dissolve mercury in double its weight of nitric acid, specific gravity 1·42. Add to the solution an equal volume of water. One c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric iodide with acetic acid.* KI 33·2 grms., $HgCl_2$ 13·5, $C_2H_4O_2$ 20 c.c., H_2O 64 c.c.

Apparatus.—1. Pipettes marked at 59·5, 60, and 60·5 c.c. 2. Sugar flasks marked at 102·4 c.c. 3. Filters, observation tubes, and polariscope. 4. Specific gravity spindle and cylinder. 5. Thermometers.

Manipulation.—1. The room and milk should be kept at a constant temperature. It is not important that the temperature should be of any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the results for analytical purposes. The temperature selected should be the one which is most easily kept constant.

2. The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required use specific gravity flask.

3. If the specific gravity be 1·026, or nearly so, measure out 60·5 c.c. into the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. of mercuric iodide solution, and fill to 102·4 c.c. mark. The precipitated albumen occupies a volume of about 2·44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1·030, use 60 c.c. of milk. If specific gravity is 1·034, use 59·5 c.c. of milk.

4. Fill up to mark in 102·4 c.c. flask, shake well, filter, and polarise.

NOTES.—In the above method of analysis the specific rotatory power of milk sugar is taken at 52·5, and the weight of it in 100 c.c. solution to read 100 degrees in the cane-sugar scale at 20·56 grms. This is for instruments requiring 16·19 grms., sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk-sugar whatever instrument is employed.

Since the quantity of milk taken is three times 20·56 grms., the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide reading by 6; if a 500 m.m. tube is used, divide by 7·5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102·4 for 60 c.c. no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarising.

Alternate Method.

The sugar may also be determined either gravimetrically or volumetrically by alkaline copper solution.

Estimation of Ash.

Evaporate to dryness in a weighed platinum dish 20 c.c. of milk from a weighing bottle, to which 6 c.c. of HNO_3 has been added, and burn at low red heat until ash is free from carbon.

THE IMPERIAL INSTITUTE.

On the 18th of the present month there took place an important gathering of friends of the Institute and representatives of the Press for the purpose of examining the progress which has been already made and considering future prospects. The visitors were conducted round the building by the Secretary, Sir Frederick A. Abel, K.C.B., F.R.S., who explained all the particulars of each department. It must be admitted that though the Institute is far from complete, yet much work, and good work, has been accomplished.

The objects of the Imperial Institute, as set forth in its Charter, are simply beyond all praise, and we can only hope that they will be faithfully and vigorously carried out. To do this, however, ample funds will be required.

The one great defect of the Institution—the non-central character of its position—is fully admitted. But it is shown that to have obtained an adequate area of ground either in the East Central or West Central districts would have encroached too far upon the funds required for building, fitting up, and organising the Institution. Hence, as the less of two evils, it shares with the Natural History Department of the British Museum a "splendid banishment" to South Kensington.

The constitution of the governing body is eminently satisfactory. Anything savouring of political partizanship has been judiciously avoided, and will, we hope, remain so in future. The only point necessary will be to carefully exclude from the governorship any persons hostile to the Colonies and to India.

The resources of the Institute, which, it must be remembered, have not been supplied by the Exchequer, amount at present to £413,000. Hence, with a due regard to the magnitude of the undertaking, the governing body did not feel at liberty to accept some of the most gorgeous and expensive plans. They adopted the designs of Mr. Collcutt, which, though by no means lacking either in convenience or even in architectural beauty, were more economical. As it is, the erection of some of the most imposing features of the building, such as the Great Hall and the principal stairway, will be postponed until the available funds permit.

The principal floor, in addition to minor features, contains the British-American, the Australasian, British-African, and Indian Conference rooms. These conference rooms form one of the most important features of the Institute. They will serve as meeting and consultation places for persons connected with, or interested in, the productions and trade of the respective groups of Colonies concerned.

The first floor comprises conference rooms for the so-called "crown colonies," commercial conference rooms, and the commercial intelligence departments.

The second-floor contains a map room, rooms for the examination of samples, and laboratories.

The ground-floor provides ample space for classified commercial samples in bulk.

We may here explain the course which a business visitor, desirous of specific information, should follow. He would first visit the Gallery, where the Index Collection and illustrations of the uses of the various products will be exhibited, and by the aid of the descriptive catalogue, or of the special hand books in course of preparation, he will easily find any particulars concerning the products of which he is in search, &c. If he wishes to know more he can then fill up a blank form with the name and reference number of the product in question, and proceed by a lift close at hand to one of the sample examination rooms on the second floor. Meantime, a box containing the bulk-sample will be brought up by lift from the store-rooms on the ground-floor. The visitors' inquiry paper will, if needful, be passed to the Commercial Intelligence Department, and returned to him with any detailed information which he may require. He will also be supplied with samples of any material which he may require for private study or experiment.

We are glad to perceive a notice that the wasteful and slovenly custom of throwing away the samples when examined will not be permitted.

Closely connected with the museum of samples is the Commercial Intelligence Department, founded on the model of the Intelligence Department of the War Office. It will systematically supply to chambers of commerce, &c., commercial information and statistics. The merchant or the manufacturer will here be able to learn where he may obtain materials or produce suitable for any given purpose, and where he may find the best demand for anything which he may have to dispose of. The sample museum and the intelligence department will be worked as much for the benefit of India and the Colonies as of the United Kingdom. These departments jointly will supply a very decided want. We have often felt pain and humiliation at perceiving that some novel product of the British Empire was brought into use in alien countries sooner than in England.

The Imperial Institute will, of course, not take any direct part in the task of education, and will not, as it was at one time feared, set on foot a new system of examination. But it will actively assist in the organisation of technical instruction at home and in the Colonies, so as to keep it on a footing, at least of equality, with that existing in alien countries. "Measures will be adopted for enabling the Enquiry Department to supply to students coming to Britain from the Colonies, Dependencies, and India the requisite information and advice to aid them in selecting their place of work and their temporary homes." Provincial industrial colleges, local commercial museums, &c., will be supplied with complete, thoroughly classified, economic collections, and with all that is new in the way of natural products, from the Colonies and India. A central department of commercial geography will form an important feature in the work of the Imperial Institute. It is to be hoped that these efforts may contribute to lighten that dense cloud of ignorance, of indifference to the Colonies and India, which is one of our weak points as a nation.

If a slight digression is permissible we should suggest a reform of our school manuals of geography. In so-called political geography the notion of "quarters of the globe" is obsolete. After the study of the United Kingdom the pupil should proceed at once and on a similar scale to a survey of India, Australia, the Dominion, British Africa, &c., and he should be taught to regard the inhabitants of all these regions as his countrymen.

We are glad to find that the study of Modern Oriental Languages is organised as a branch of the Institute. The daughters of the late Colonel Ouseley, of the Bengal Army, have endowed in his memory three scholarships in

Arabic and Persian, each one of the value of not less than £50 yearly.

An Exhibition of Indian Metal Work has now been opened at the Institute. Its nucleus will consist of a representative collection formed by H.H. the Maharaja of Jeypore.

We think that any British subject worthy of the name who carefully examines into the subject will give the Imperial Institute his most earnest support.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 2nd, 1892.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MR. WALTER N. EDWARDS was formally admitted a Member of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Duxbury, Richmond Terrace, Darwen, Lancashire; Thomas Gray, 16, Craigmore Terrace, Dowanhill, Glasgow; Samuel C. Hooker, Philadelphia, U.S.A.; Samuel Jackson, Nether Thong, Huddersfield; Charles Spackman, Sileby, Loughborough; Frederick William Westaway, 8, Ayton Road, Stockwell, S.W.

Of the following papers those marked * were read:—

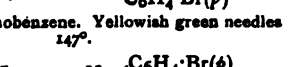
26. "*Ethylene Derivatives of Diazoamido-Compounds.*" By R. MELDOLA, F.R.S., and F. W. STREATFEILD, F.I.C.

In the same way that alkyldiazoamides can be prepared by the action of alkyl haloids on diazoamides dissolved in alcohol, together with the calculated quantity of potassium or sodium hydroxide (*Trans.*, xlix., 624; li., 102 and 434; liii., 664; lv., 412; and lvii., 784), the authors find that ethylene derivatives can be obtained by the substitution of ethylene dibromide for the alkyl haloid. The products thus obtained have the general formulæ—

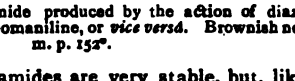
Normal ethylenediazoamide. Mixed ethylenediazoamide.

In this preliminary note it is desired only to call attention to the existence of these compounds; their detailed study will be undertaken as soon as possible. The following have been thus far prepared:—

From diazoamido-*p*-toluene. Dull orange needles; m. p., 116—117°.



From diazoamido-*p*-bromobenzene. Yellowish green needles m. p., 147°.



From the mixed diazoamide produced by the action of diazotised metanitraniline on parabromaniline, or *vice versâ*. Brownish needles, m. p. 152°.

The alkylenediazoamides are very stable, but, like the alkyl derivatives, are resolved by prolonged contact with strong chlorhydric acid at ordinary temperatures; the products of decomposition have not yet been investigated, but special interest attaches to their examination. The normal compounds may be expected to give rise to—

and the mixed compounds to $X{\cdot}N_2Cl$ and $Y{\cdot}N_2{\cdot}Cl$, together with a mixed substituted ethylenediamine of the type—

*27. "*The Action of Light on Silver Chloride.*" By H. BRERETON BAKER, M.A.

The small loss in weight which silver chloride undergoes on exposure to light has led the author to investigate whether oxygen is absorbed at the same time that chlorine is evolved, Robert Hunt having long ago stated that such an absorption does take place. In the first experiments silver chloride was exposed to light in a bulb connected with a long tube standing over potassium hydrate solution; a very noticeable absorption took place. Similar experiments with oxygen, instead of air, gave similar results, showing that oxygen was the gas absorbed. Attempts were then made to find in what proportions the elements silver, chlorine, and oxygen were combined in the darkened substance, but so little of the dark substance was produced (less than 0·1 grm. in 50 grms. of unaltered chloride) that a direct analysis was found to be impossible, and an indirect method was adopted.

In the first experiments to ascertain the formula, the evolved chlorine was absorbed by potassium iodide, and the iodine which it liberated was determined; the silver was determined by treating the blackened chloride with strong ammonia, and weighing the residual metal; and the oxygen by treating the dark substance with pure chlorine and measuring the oxygen evolved. The results of one such experiment were as follows:—

	Found.	Calculated for Ag_2ClO.
Ag	78·94	80·75
Cl	14·25	13·27
O	6·81	5·98

Other experiments were made in which the oxygen absorbed and the chlorine evolved were determined in the same apparatus. The following are some of the results:—

	Oxygen absorbed.	Chlorine evolved.
I.	1 atom.	0·70 atom.
II.	1 „	1·26 atoms.
III.	1 „	1·12 „
IV.	1 „	1·26 „

The discrepancy of the results is attributable partly to the difficulty of working with a substance which can only be obtained in small quantities, and then in admixture with a large quantity of unaltered silver chloride, and to the fact that if the analyses are not immediately performed, the determination of the formula becomes uncertain, owing to the darkened substance turning white when kept in the dark, a fresh absorption of oxygen taking place, so that probably another oxychloride is formed.

It was found that the thoroughly dried darkened substance, free from oxygen, gave an amount of water when reduced in pure hydrogen which corresponded to an amount of oxygen differing from that determined by other methods by less than 1 per cent.

If the darkened substance be really an oxychloride, it should not be produced in absence of oxygen. This was found to be the case, no darkening being observed in a vacuum or in carbon dioxide. Likewise no darkening was produced when silver chloride was exposed under pure dry carbon tetrachloride. It is to be noted, however, that carbon tetrachloride, unless carefully purified, contains substances, such as alcohol, carbon bisulphide, &c., which cause reduction of silver chloride and the deposition of black silver or silver sulphide, which darkening has hitherto been confounded with the darkening which takes place in air.

Lastly, when darkened silver chloride is boiled with pure potassium chloride, the whole dissolves, silver chloride being found in the solution together with potash

the production of alkali seems to prove that oxygen is present in the darkened substance in the combined state.

28. "*The Estimation of Slag in Wrought Iron.*" By A. E. Barrows and Thomas Turner.

It is known that in puddling cast-iron comparatively rich in non-metallic elements, the yield of puddled bar is greater than with less impure materials, but the loss on re-heating and rolling into finished iron is also greater. It has been contended that this difference is due to intermingled slag.

The authors prepared four samples of iron, viz., best bar, best sheet from the same bar, common bar, and common sheet from the same. Pig-iron of known composition was used; the yield of common puddled bar was 6·5 per cent greater than the other, but the loss in re-heating was also 1·5 per cent greater, leaving a balance of 5 per cent in favour of the common iron. The composition of the samples was as follows:—

	Best.		Common.	
	Bar.	Sheet.	Bar.	Sheet.
Carbon	0·060	0·035	0·045	0·032
Silicon	0·228	0·168	0·275	0·221
Phosphorus ..	0·178	0·175	0·589	0·390

These results show that the silicon is equally, and very slightly, reduced in each case, while the phosphorus was much reduced in common iron, and but scarcely affected in best. This does not favour the view that much more slag is removed in one case than the other.

The authors attempted to estimate the slag by combustion in chlorine, a method already employed by one of them for cast-iron (*C. S. Trans.*, xlv., 263), but they found that the slag was attacked by the chlorine, the action taking place quite sharply at a scarcely visible red heat. A considerable number of iron ores and slags were examined, and it was found that action takes place in the sense of the equation $3FeO = Fe_3O_3 + Fe$, the iron being removed by volatilisation as ferric chloride.

This action was unexpected, and, so far as the authors are aware, has not been observed before; Deville has, however, shown that when ferrous oxide is heated in hydrogen chloride, it yields magnetic oxide of iron and ferrous chloride (*Compt. Rend.*, liii., 199).

By dissolving the iron in a cold solution of sodium copper chloride, the authors have obtained the following values:—

	Best.		Common.	
	Bar.	Sheet.	Bar.	Sheet.
Slag per cent	3·83	2·58	3·85	2·85
Loss on re-heating ..	1·25 p.c.		1·00 p.c.	

This method requires to be further examined and checked by other processes before the results can be accepted, but they are at least a fairly close approximation to the truth. Though the chlorine process is not suited for slags containing iron, it appears to be correct for cast-iron analysis, since the slag from the blast furnace seldom contains more than a trace of iron.

The authors conclude that for practical purposes the weight of slag in best and common iron may be taken as identical, and that on re-heating and rolling, each loses about the same weight of slag. The additional loss noticed on re-heating impure iron is due chiefly to the elimination of phosphorus, probably in the form of ferrous phosphate.

29. "*Corydaline.*" II. By James J. Dobbie, M.A., D.Sc., and Alexander Lauder.

In confirmation of the formula proposed in their first paper (*C. S. Trans.*, 1892, 244), the authors give the results of analyses of the bromhydride and ethylsulphate ($C_{22}H_{20}NO_4 \cdot C_2H_5HSO_4 + H_2O$). The latter compound is obtained by adding sulphuric acid to an alcoholic solution of corydaline, evaporating the solution to a syrupy consistency and treating with water, when crystals of the salt immediately separate out. The ethylsulphate easily dissolves in hot water, from which it crystallises, on cooling, in colourless prisms.

The alkaloid examined by the authors is identical with that obtained by Adermann (*Diss. Dorpat*, 1890; Abstr., 1891, 1266) from the roots of *Corydalis cava*, by extracting with alcohol and exhausting the alcoholic solution with benzene. The two alkaloids agree in composition, in solubility, in melting-point, in their action on polarised light (dextrorotatory), and in the character of the salts which they form. On the other hand, it is quite distinct from hydroberberine, with which Adermann believed his alkaloid to be identical, or at least isomeric.

When treated with concentrated solution of hydrogen iodide, one molecular weight of corydaline gives four molecular proportions of methyl iodide and the iodhydride of a new alkaloid which has the formula $C_{18}H_{21}NO_4,HI$. The alkaloid is obtained from this salt by the addition of ammonia or potassium hydroxide, and dissolves in excess of either agent. It possesses powerful reducing properties, and dissolves in alcohol, forming a deep red-coloured solution. The conclusion that the four oxygen atoms in corydaline are united to methyl groups is confirmed by the failure to obtain any definite action with phenylhydrazine or phosphorous pentachloride.

30. "*The Action of Bromine on Allylthiocarbimide.*" By Augustus E. Dixon, M.D.

According to Proskauer and Sell (*Ber.*, ix., 1262), bromine and phenylthiocarbimide interact, yielding an orange-red solid dibromide in accordance with the equation—

$$3C_6H_5NCS + 2Br = \begin{matrix} C_6H_5 \cdot NC \cdot SBr \\ C_6H_5 \cdot NC \cdot SBr \end{matrix} > S + C_6H_5 \cdot NC;$$

and it is further stated that the action on ethyl- and allyl-thiocarbimides leads to similar results. But no data of any kind are given in support of the latter statement; the author has now investigated the case of allylthiocarbimide.

Under the conditions of his experiments, viz., operating in chloroform solution, 1 mol. bromine readily unites with 1 mol. thiocarbimide, yielding dibromopropylthiocarbimide, an oily liquid, insoluble in water, soluble in alcohol, having at 17°/17° a rel. den. of 1·9712, and decomposing on distillation at ordinary pressure.

When treated with aniline it does not afford dibromopropylphenylthiourea, but the two substances interact with elimination of HBr, forming a compound of the formula $C_{10}H_{11}BrN_2S$, probably *n*-phenylbromotrimethylene-ψ-thiourea. This substance is insoluble in water, but soluble in alcohol; it melts at 103—104° (uncorr.), and is not desulphurised either on the addition of $AgNO_3.2NH_3$ or by boiling with an alkaline solution of a lead salt.

31. "*The Hydrolytic Functions of Yeast.*" Part I. By James O'Sullivan.

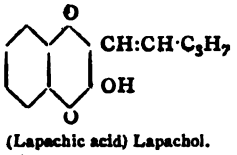
It is generally stated, on the authority of Berthelot, that the water in which yeast has been washed possesses, like yeast itself, the power of hydrolysing cane sugar, and that the active substance can be precipitated from the solution by means of alcohol. In the present communication it is shown that *healthy* yeast yields none of its invertase to water in which it is washed; and that when it is placed in contact with sugar, hydrolysis is effected solely under the immediate influence of the plasma of the cell, no invertase leaving the cell while hydrolysis is taking place.

After describing his mode of obtaining a healthy yeast, the author gives an account of the difficulty met with in removing the cells from the liquid in which they were suspended; although bright liquids free from organisms were obtained by adding aluminium hydrate, finings, or gypsum before filtering, such substances were found to retard the activity of the invertase, and therefore could not be used. Ultimately the object was obtained by shaking up the yeast and water with filter-paper pulp before filtering.

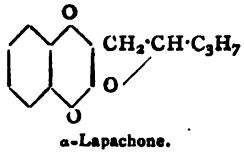
A detailed account is given of experiments carried out under various conditions, which show that water which had been in contact with highly active yeast for various times had no hydrolytic power, although on the addition of a mere trace of invertase the solution at once became active. The author therefore concludes that the resolution of cane sugar under the influence of yeast is entirely due to zymic hydrolysis.

*32. "*The Constitution of Lapachic Acid (Lapachol) and its Derivatives.*" By SAMUEL C. HOOKER, PH.D.

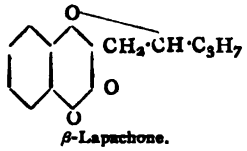
Lapachic "acid" is found in a crystalline state in the grain of a number of South American woods, the lapacho tree, from which it derives its name, growing plentifully in the Argentine Republic; the author has obtained his material chiefly from Surinam greenheart. Paterno, in 1882, came to the conclusion that lapachic acid (lapachol) was a homonucleal *amylenehydroxynaphthaquinone*, and he subsequently expressed the view that it was an α-quinone derivative, because lapachone, a neutral isomeric substance, into which it is converted by sulphuric acid, in his opinion resembled α- rather than β-naphthaquinone. The author shows that although Paterno correctly regarded lapachol as an α-quinone, his reason for doing so was wrong, as lapachone is derived from β-naphthaquinone. He proposes to term lapachone β-lapachone, to distinguish it from the isomeric pale yellow substance —a true α-quinone derivative—α-lapachone, which is obtained on treating lapachol with concentrated muriatic acid. The nature of the changes involved in the formation of α- and β-lapachones from lapachol is fully discussed in the paper, the formulæ assigned to them being as follows:—



(Lapachic acid) Lapachol.



α-Lapachone.



β-Lapachone.

It is shown that Paterno's isolapachone in reality contains less hydrogen than the lapachones, and that it is doubtless a β-naphthaquinonepropylfurfuran.

PHYSICAL SOCIETY.

Ordinary Meeting, June 10th, 1892.

MR. WALTER BAILY, M.A., Vice-President, in the Chair.

DR. GLADSTONE read a paper "*On some Points connected with the Electromotive Force of Secondary Batteries*," by himself and W. HIBBERT.

The communication includes replies to certain questions raised by M. Darrieus in a paper read before the Société Internationale des Electriciens on May 4, 1892, and to the views expressed by Prof. Armstrong and Mr. Robertson in the discussion on a paper by the present authors read before the Institute of Electrical Engineers on May 12 and 19. It also contains an account of their recent experiments on the subject.

M. Darrieus agrees with Prof. Armstrong and Mr. Robertson that the large E.M.F. immediately after change is due to persulphuric acid, and opposes the ordinary theory that the ultimate product of discharge is lead sulphate at both plates, so far as the positive plate is concerned. The authors attribute the finding of large quantities of lead oxide by M. Darrieus to difficulties in analysis, for it is not easy to imagine that oxide of lead could remain as such in presence of sulphuric acid. They have also shown that the changes of E.M.F. during charge and discharge coincide fairly well with those obtained by putting Pb and PbO_2 plates in different strengths of acid, and conclude "that the changes of E.M.F. depend on the strength of the acid that is against the working surface of the plates." Prof. Armstrong and Mr. Robertson disagree with the authors' views, and suppose that the sulphuric acid used was contaminated with soluble peroxides; and they also believe that H_2SO_4 itself takes part in the reactions. As regards the first objection, the authors see no reason why the traces of soluble peroxide (if any) on the plates should always vary in amount with the strength of the fresh acid in which the plates are dipped. The second point they leave an open question. In reply to the criticism on the summation of the two curves obtained respectively with two lead plates and two lead peroxide plates in acids of different strengths, they point out that the resulting curve coincides both in shape and magnitude with that determined when Pb and PbO_2 plates were placed in different strengths of acid. Whilst admitting the possibility of the lead supports having some influence on the result, they cannot conceive that such large and uniform differences as those given in their paper can be due to accidental operations of local action.

To show that the increase of E.M.F. does not depend on the presence or absence of persulphuric acid, the authors have tested the E.M.F. of a Pb and a PbO_2 plate, free from soluble oxides, in sulphuric acid of 15 per cent strength; a porous diaphragm being between the plates. The E.M.F. was 1·945 volts. After adding 1 per cent of persulphate of potassium to the liquid surrounding the PbO_2 plate, the E.M.F. was unaltered, whilst putting the Pb plate in the same liquid only reduced the E.M.F. to 1·934. Experiments had also been made on cells with phosphoric acid of different strengths instead of sulphuric acid. Changing the density from 1·05 to 1·5 raised the E.M.F. 0·176 volt, whilst calculations from Lord Kelvin's law gave 0·171 volt. In this case they consider that no acid analogous to persulphuric acid could be present. They also find that the effects of charging and repose on the E.M.F. of phosphoric acid cells are quite analogous to those obtained with sulphuric acid. The researches are being extended chiefly on the thermo-chemical side.

Prof. AYRTON thought that there was no question that the strength of acid had much to do with the changes of E.M.F. The point at issue, he considered, was whether the changes were direct effects of the strength of acid, or due to secondary actions brought about by alterations in strength.

Mr. E. W. SMITH said Mr. Robertson and himself were repeating the authors' experiments with two PbO_2 plates without any grid. They had obtained results analogous to those mentioned in the paper, but the true explanation of the effects was still to seek.

Mr. W. HIBBERT contended that the soluble oxides referred to by Prof. Armstrong and Mr. Robertson were not present is their experiments. They had also proved that changes in acid strength altered the E.M.F., whilst presence of persulphuric acid did not.

Dr. GLADSTONE, in reply, said they also were making experiments without grids, but had not made sufficient progress to discuss them at present. Mr. Hibbert and himself believed the effects of local action inconsiderable, whilst Messrs. Armstrong and Robertson thought them very important. He hoped that ere long the points would be settled conclusively.

A paper on "*Workshop, Ballistic, and other Shielded Galvanometers*," by Prof. W. E. AYRTON, F.R.S., and T. MATHER, was read by Prof. AYRTON.

The galvanometers described were of the type having movable coils and fixed magnets, the advantages of which are well known. In designing the ballistic instruments, their aim had been to obtain sensibility and portability, combined with being screened from external influ-

ences, for it was often desirable to measure the magnetic fluxes and fields in dynamos by apparatus near the machines. One of the improvements adopted was the narrow coil described in a paper "On the Shape of Movable Coils, &c.," read before the Society in 1890. Such coils are particularly advantageous for ballistic instruments; for not only can greater swings be obtained by the discharge of a given quantity of electricity through such a coil than with ordinary shaped coils, when the periodic times are the same, but even when the same control is used, the same length of wire in the coil, and suspended in the same field, the narrow coil is more sensitive to discharge than coils of any other shape. Another improvement was the use of phosphor bronze strip for the suspensions instead of round wire. For a given tensile strength, both the control and the subpermanent set could be diminished by using strip.

In February, 1888, the authors made a d'Arsonval of the ordinary type as a ballistic instrument, and found that although it was suitable for comparing condensors, for induction measurements the damping was excessive unless the resistence in the circuit was very large; this greatly reduced the sensitiveness. In 1890 they tried one of Carpentier's milliampèremeters as a ballistic instrument, but found it unsensitive. A narrow coil instrument made in the same year was found to be sensitive for currents, but as the coil was wound on copper to get damping, it was not suitable for ballistic work. In January, 1892, a somewhat similar instrument was constructed for ballistic purposes, and was found very sensitive and convenient. Although the coil had only a resistance of 13 ohms, one microcoulomb gave a swing of 170 divisions on a scale 2000 divisions distant, the periodic time being 2·7 seconds. The instrument could be used near electromagnets or dynamos, and was so sensitive that for ordinary induction measurements very large resistances can be put in series with it, thus reducing the damping to a very small amount. On the other hand, the coil could be brought to rest immediately by a short circuit key. It had the further advantage that it was not necessary to redetermine its constant every time it was used. The chief disadvantage of such instruments was the variable damping on closed circuits of different resistances. This could, however, be overcome by arranging shunts and resistances so that the external resistance between the galvanometer terminals was the same for all sensibilities.

A portable ballistic instrument, intended for workshop use, was next described. This had a narrow coil and a pointer moving over a dial whose whole circumference was divided into 200 parts. The instrument had been designed to give a complete revolution for a reversal of a flux of two million C.G.S. units, but the pointer could turn through two or more revolutions. To test stray fields, a test coil with a total area of 10,000 square centimetres is used, and has a trigger arrangement for suddenly twisting it through two right angles. The instrument then reads off directly the strength of field in C.G.S. lines. To vary the sensitiveness in known proportions resistances are employed.

Referring to the improvements made in movable coil instruments since January, 1890, when a paper on "Galvanometers" was read before the Society by Dr. Sumpner and the present authors, Prof. Ayrton said Mr. Crompton had greatly increased the sensitiveness of Carpentier's instruments by suspending the coils with phosphor bronze strip. Mr. Paul had brought out a narrow coil instrument which combined the advantages of portability, deadbeatness, quickness, and sensibility. Specimens of these instruments were exhibited. The narrow coils are enclosed in silver tubes which serve to damp the oscillations. Such a coil is suspended within a brass tube which also forms the mirror chamber, and slides down between the poles of a circular magnet fixed to the base. To damp the coil, a plug mounted on a slotted spring passes through a hole in the brass tube. A tube can be taken out and replaced by another containing a coil of different resistance in a few seconds. An instrument of this kind, with a coil of 300 ohms, gave 95 divisions per microampère, and the damping on open circuit was such that any swing was $\frac{1}{15}$th of the previous one.

On comparing recent instruments with those mentioned in the paper on galvanometers above referred to, a distinct improvement is apparent; for their sensitiveness is, for the same resistance and periodic time, as great as that of Thomson instruments.

Prof. Perry remarked that the forces dealt with are extremely small.

Mr. Swinburne thought that ballistic galvanometers might be regarded as instruments indicating the time-integral of E.M.F. rather than quantity. Illustrating his meaning by reference to dynamos, he said that if two machines arranged as dynamo and motor were joined by wires, then if the armature of the dynamo were turned through any angle, that of the motor would move through the same angle supposing friction, &c., eliminated. Speaking of figures of merit, he pointed out that the power consumed was the important factor.

Prof. S. P. Thompson enquired what was the longest periods yet obtained with narrow coil instruments. The decay of magnetism in large dynamos was so slow that very long periods were required. He himself had used a weighted coil for such measurements. He also wished to know why the figures of merit were expressed in terms of scale divisions on a scale at 2000 divisions distance, instead of in angular measure or in tangents.

Mr. E. W. Smith asked what was the length of strip required to prevent permanent sets when the deflection exceeded a revolution.

Mr. A. P. Trotter thought that in testing magnetic fluxes by the workshop ballistic instrument, the test coil might be left in circuit instead of putting in another coil. He wished to know what error was introduced by the change of damping caused by the resistance of the circuit not being quite constant.

In his reply, Prof. Ayrton said Mr. Boys had pointed out that the scientific way to lengthen period was not by weighting the coils or needles, but to weaken the control. Periods of five seconds had been obtained. At present it was not easy to obtain longer periods, owing to difficulties in obtaining sufficiently thin strip, and to the magnetism of materials.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, June 13, 1892.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Harry Stanley Giffard; William John Heath; Mrs. Lawson; Alexander Morrison, M.D.; The Hon. William Frederick Danvers Smith, M.P.; W. Bezley Thorne, M.D.; and Captain R. H. C. Tufnell.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

The special thanks of the Members were returned for the following donations for carrying on investigations on liquid oxygen:—Mrs. Bloomfield Moore, £80; Sir David Salomons, Bart., £50; Charles Hawksley, £50.

Bacteriology.—Mr. W. Heinemann will publish in the early autumn a "Manual of Bacteriology," by Dr. A. B. Griffiths. It is essentially a work for the laboratory, and will be of use to chemists, sanitarians, brewers, medical men, agriculturalists, and others. It will be illustrated with 58 figures

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 23, June 7, 1892.

Products of the Residual Life of the Tissues, and in particular of the Muscular Tissue separated from the Living Being.—Arm. Gautier and L. Landi.—Fresh meat, even when protected from any change due to external ferments is gradually acidified. This change is due on the one hand to the formation of a small quantity of butyric and acetic acid; on the other to an incipient peptonisation of the albumenoids, and thirdly, to the formation of a little nucleine. There is formed a soluble albumenoid or myoalbumen,—a substance presenting all the characters of the caseine of milk. Nearly 9 per cent of the albumenoids of fresh meat disappear and are changed into basic substances, alkaloids. The gelatinisable matters, peptones, and extractive substances do not appreciably vary in proportion.

New Methods of the Formation of Certain Substituted Imides.—A. Haller.—Phenylcarboimide, in consequence of its ready conversion into symmetric diphenyl-urea, is a dehydrating agent, and may in some cases be employed as such. The symmetrical disubstituted ureas readily form with the anhydrides dicarboxylic acids, substituted imides.

Basic Zinc Nitrates.—J. Riban.—The author has caused nitric acid, diluted with about an equal volume of water, to act upon pure zinc. There is first formed neutral zinc nitrate, but if boiled in presence of an excess of the metal there is produced a white precipitate of a basic salt, which is filtered off. The filtrate as it gradually cools becomes turbid, and yields successive deposits which are separated by filtration. The first portions deposited are generally formed of rhombic tables and needles; the subsequent deposits consist of very short needles grouped in stars. The composition of the latter portion is $6ZnO,N_2O_5,8H_2O$. A compound may also be obtained of the composition $6ZnO,N_2O_5.7H_2O$, having lost 1 mol. of water in the hot liquid.

On the Permolybdates.—E. Péchard.—The author has obtained and described the sodium, magnesium, and barium salt, and the permolybdates of the heavy metals. The existence of a peroxygenated acid of molybdenum is beyond doubt.

The Reproduction of Leucite.—A. Duboin.—The author has reproduced leucite by various reactions effected in presence of melted potassium fluoride, an excess of which acts as the solvent.

Contributions to the Study of Mineral Waters and their Preservation.—P. Parmentier.—The author has sought for means to obtain for analysis and research a water identical with that of the spring, and to operate upon well-defined liquids. With many chemists he contends that the analysis of a water should include all the principles present in the water at the moment when it flows clear from the spring. Others only take into consideration the clear portion contained in the bottles, the sediments being rejected. He considers that the mineral waters of Central France take their rise in an atmosphere of *pure* carbonic acid, and that no oxygen should come in contact with the bottles or the water during the process of bottling.

Fixation of Iodine by Starch.—Gaston Rouvier.—The compounds obtained by the author and by Mylius has the composition $(C_6H_{10}O_5)_4I$, or $(C_6H_{10}O_5)_8I_2$.

Preparation and Formation-Heat of Monosodic Resorcine and Hydroquinone.—M. de Forcrand.—A thermo-chemical paper not adapted for useful abstraction, and not possessing sufficient interest for insertion in extenso.

Mechanical Determination of the Boiling-Points of Alcohol and of Acids.—G. Hinrichs.—This paper, which is purely mathematical, requires the accompanying diagram.

Thermic Study of the Bibasic Organic Acids. Methyl-malonic and Methyl-succinic Acids. Influence of Isomerism.—G. Massol.—The author's conclusions are that the methyl-malonic or iso-succinic acid evolves more heat than its isomer succinic acid, and that it approximates to malonic acid. Methyl-succinic or ordinary pyro-tartaric acid evolves as much heat as succinic acid. These facts seem to follow from the consideration that in these acids, taken two by two, the distance of the two groups is the same.

An Oxidation-Product of Starch.—P. Petit.—On treating 4 parts of starch containing 20 per cent of water with 5 parts of the pure nitric acid of commerce, the author obtains a compound of the composition $C_5H_6O_5$. This substance, if thrown in fine powder into a concentrated solution of phenylhydrazine acetate, yields, at about 60°—70°, a crystalline hydrazone.

Organo-metallic Compounds of the Aromatic Acetones.—E. Louise and Perrier.—The authors make known a new property of the aromatic acetones, that of combining with anhydrous metallic chlorides to form solid compounds of various colours, sometimes amorphous, but more frequently crystalline. One of the authors has obtained by the method of Friedel and Crafts, but with the intervention of these new compounds, a number of crystalline acetones. They also propose to examine if other halogenous metallic salts possess the same properties as aluminium and iron chlorides, and to ascertain which among the possible isomeric acetones yield by preference organo-metallic compounds.

The Chloro-Derivatives of the Isobutylamines.—A. Berg.—The author has obtained and described monochlorisobutylamine, dichlorisobutylamine, and chlorodiisobutylamine. He has also studied the action of alcoholic soda and of potassium cyanide upon chlorodiisobutylamine.

Researches on the Ptomaines in Certain Infectious Diseases.—A. B. Griffiths.—The author has obtained the ptomaine of glanders, to which he ascribes the formula $C_{15}H_{10}N_2O_6$, and that of pneumonia $C_{20}H_{26}N_2O_3$. The former of these bases is poisonous; neither of them is found in normal urine.

MISCELLANEOUS.

The Atomic Weight of Oxygen.—Mr. R. Lehfeldt writes as follows in *Nature*:—"I notice that Lord Rayleigh gives the following summary of results on the atomic weight of oxygen:—

Dumas,	1842	.. ..	15·96
Regnault,	1845	.. ..	15·96
Rayleigh,	1889	.. ..	15·89
„	1892	.. ..	15·882

showing the remarkable fact that the atomic weight has been steadily decreasing for the last fifty years. I would suggest, as the explanation of this, that the increased population of the world, together with the great consumption of coal, have caused great wear and tear of these atoms, so that they are now mostly deficient in weight. It would seem, in fact, desirable that a Congress of chemists should be called to consider the question of providing for the renovation of the oxygen supply, and issuing trustworthy atoms of the standard weight, 16, as sealed patterns.—Firth College, Sheffield, June 3.

Physiology of the Invertebrata.—Messrs. L. Reeve and Co. have just published an important work, "The Physiology of the Invertebrata," by Dr. A. B. Griffiths, F.R.S.E., F.C.S. (demy 8vo., pp. 494, 81 figures). This work treats of the applications of chemistry and physics to the solution of biological problems.

MEETINGS FOR THE WEEK.

WEDNESDAY, 29th.—Society of Arts, 4. (Anniversary).
FRIDAY, July 1st.—Geologists' Association, 8.
—— Quekett Club, 8.

BAGILLT, FLINTSHIRE.

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ONE EQUAL UNDIVIDED MOIETY of and in the Shipping Wharves, Flushing Pool, and Land adjoining and near to and adjoining the last-described premises, containing 3a. 2r. 29p. or thereabouts, and coloured red on the sale plan; and of and in the gutters, openings, and conveniences for shipping adjoining thereto, jointly used for the purposes of the works of the vendors, Messrs. Newton, Keates, and Company, and of Messrs. Walker, Parker, and Company, the owners of the other moiety.

The above-mentioned Property will be sold subject to certain rights, which will be fully set out in the particulars of sale.

The Lessees' Interest in the entirety of a Piece of Land adjoining on the easterly side of a portion of the above secondly described Premises, containing 0a. 1r. 32p. or thereabouts, and coloured brown on the sale plan, leased to the vendors by the Board of Trade for a term of 31 years from the 29th of September, 1868, at a rent of 6s. per annum.

ONE EQUAL UNDIVIDED MOIETY of the Tenant's Interest in Two Pieces of Land, one on either side of Bagillt Gutter, containing together 1a. 0r. 20p., and coloured green on the sale plan, held by the vendors from the Dee Conservancy Board, under an annual tenancy at a rent of £25 per annum, of which Messrs. Walker, Parker, and Co., the owners of the other moiety, pay half.

The above lot affords a rare opportunity to a company desirous of acquiring premises whereon to carry on an extensive business, having regard to its situation and the facilities the property affords in securing access both to the railway and the River Dee, and for the deposit of waste. There are collieries in the immediate neighbourhood, where coal, slack, and coke can be obtained at pit prices. Vessels drawing 12 feet of water can come up the Bagillt Gutter on about an 18 feet tide.

LOT 2.

A FREEHOLD ROAD running from the main road leading from Flint to Holywell to the Bagillt Station, containing 0a. 0r. 24p. or thereabouts, and coloured purple on the sale plan. This road will be sold subject to the rights affecting it, and the purchaser will be entitled to a sum of £5 per annum, payable by the London and North Western Railway Company, for the right of user of a portion of it, and to a sum of 7s. 6d. a year, payable by Mr. Samuel Davies or his successors, in title for the right of user of another portion of it.

This lot will also be sold subject to the purchasers of Lots 3 and 4 having the right of user of the whole of the road with or without horses, carts, or carriages, but subject to their respectively maintaining and repairing in a proper manner one-half of the road co-extensive with the portions of their respective lots fronting such road.

LOT 3.

Two COTTAGES and GARDENS, in the occupation of Thomas Rowland and John Jones, containing 0a. 0r. 13p., adjoining the last-mentioned lot, and with the right to use such mentioned lot with or without horses, carts, and carriages, but subject to the purchaser maintaining and repairing in a proper manner one-half of the last-mentioned lot co-extensive with the frontage of this lot.

LOT 4.

Four COTTAGES and GARDENS at Pen-y-bont, and adjoining Lot 2, adjoining the main road leading from Flint to Holywell, in the several occupations of Robert Williams, William Kendrick, John Roberts, and Elizabeth Pickstock, together with the Garden adjoining in the occupation of Elizabeth Pickstock, containing in the whole 0a. 1r. 7p.

This lot has an extensive frontage of upwards of 100 feet to the main road.

LOT 5.

A COTTAGE GARDEN and PREMISES, with valuable Building Land adjoining, having a frontage to the township road, containing in the whole by admeasurement 4a. 2r. 7p. or thereabouts, edged round with the colour vermillion on the sale plan, and now in the holding of John Hughes.

Under and included in this lot there are several seams of coal; the five-yard coal has been worked and the three-yard coal partly worked, but it is believed there are several other seams still unworked.

If Lot 5 is not sold it will then be divided and offered in 13 suitable building lots as shown on the plan and in the particulars.

Plans with detailed particulars as to each Lot are in preparation, and will shortly be published; in the meantime any further information may be obtained on application to Mr. HENRY S. WHALLEY, Land Surveyor, 90, Northgate Street, Chester; Mr. T. HUGHES, Copper Works, Greenfield, Holywell; Messrs. KELLY & KEENE, Solicitors, Mold; or the AUCTIONEERS, Chester.

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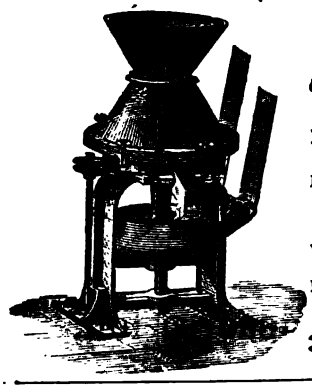

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